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DECEMBER, 1936

NUMBER 12

A METHOD OF MEASURING ABSORPTION COEFFICIENTS FOR X-RAYS BY MEANS OF A TRI-ELECTRODE IONIZATION CHAMBER¹

BY G. A. WRENSHALL² AND E. L. HARRINGTON³

Abstract

A balance method of measuring absorption coefficients for X-rays in absorbing media, using a new form of sectorized discs for determining alterations in intensity and an ionization chamber containing three electrodes, has been developed. The new arrangement makes possible a simplification of the apparatus, a complete elimination of certain sources of error, and very direct calculations of the results. A curve is included in this report to indicate the accuracy routinely attainable.

Introduction

Of the different methods offered for the accurate measurement of X-ray absorption coefficients at definite wave-lengths, nearly all involve the use of some form of the Bragg X-ray spectrometer. Those employing this instrument generally depend on magnitudes of deflections or on a balance of some type. This report deals with the development of a balance method which is essentially a modification of those of Wingårdh (3) and of Stoner and Martin (2).

Wingårdh employed a double Bragg spectrometer arrangement by which he balanced two beams of X-rays, the one against the other, one beam entering each half of the double spectrometer. A pair of rotating sectors, made of heavy brass, was used to cut down the intensity of one beam by an amount necessary to make it equal to that of the other beam which was reduced in intensity after it had passed through the absorbing film. The adjustment for balance was found by means of a quadrant electrometer used as a null instrument. Stoner and Martin employed the same principle as Wingårdh but used a pair of semicylindrical ionization chambers set one above the other on a single Bragg spectrometer, in place of the usual cylindrical ionization chamber. This modification greatly simplified the experimental requirements and had certain other advantages over the method used by Wingårdh.

While each of these methods involve uncertainties, which will be pointed out later, the principle of the balance method has some very distinctive advantages over the methods involving the determinations of magnitudes

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or rates of deflections, among which are the following. The balance method eliminates all uncertainties as to scale calibrations, or changes in leakage or capacities with deflections. Stray radiations, whether constant or variable, are unlikely to affect observations made by a balance method since their effects in the two chambers are in general equal in magnitude but opposite in sign, though they might prove to be a serious matter in the case of a method involving deflections in successive runs. The same can be said with respect to the intensity of the X-ray beam itself, for ordinary variations have no effect in the former case and are intolerable in the latter. While saturation currents are always desirable, though never fully obtained, the results are immaterially affected by this factor when a method involving a balance is employed but may be rendered uncertain when they depend on deflections. In short, so many of the sources of uncertainty or of error, as well as certain experimental difficulties inherent in methods involving deflections, are eliminated by methods involving balanced conditions that it seemed worth while to attempt certain improvements in the latter.

Experimental

The general arrangement of the apparatus is represented diagrammatically in Fig. 1. The X-ray beam passing out through a window in the lead bowl surrounding the X-ray tube is further limited by slits S_1 and S_2 ; and of the

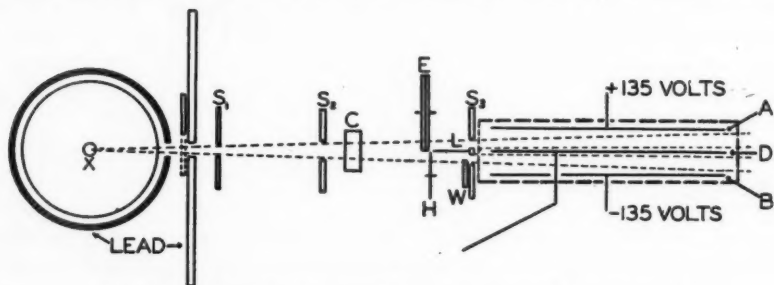


FIG. 1. A schematic diagram of the arrangement of the apparatus (vertical section but not drawn to scale).

narrow band, thus defined, the portion reflected by the crystal of rock salt, C , when the latter is properly adjusted, will be monochromatic within limits fixed by the widths of the slits and their location. The upper half of the reflected band then passes through the sectored discs, E , used to modify its intensity, while the lower passes through a foil of the metal, H , of which the absorption coefficient is to be measured. A lead cross bar, L , gives definite limits to the two halves and also provides a shadow for the central electrode of the ionization chamber. After passing through another slit, S_3 , the two halves, now reduced in intensity, finally enter the twin or tri-electrode ionization chamber, the latter being so adjusted that no part of either half of the residual beam can strike either an electrode or the brass wall of the chamber.

Its construction and the electrical arrangements are such that the electrometer, used as an indicating instrument, shows no deflection when the two parts of the beam entering the chamber are of equal intensities.

Proper alignment of slits, rotating sectors, absorbing foils, and of the ionization chamber and X-ray target were secured through the use of a cathetometer. The slit widths were set at about 0.3 mm., and were adjusted with such precision that the width of any slit did not vary more than 0.003 mm. from one end to the other.

The general steps taken to secure a balance include the following. The X-ray tube was run continuously until it reached such a steady state that a constant delivery could be expected. Then the necessary potentials were applied to the plates of the ionization chamber, and any slight drift of the electrometer needle was balanced out by means of a weak γ -ray source placed at a suitable position relative to the ionization chamber. With the discs stationary and their open sectors in line with the slit and the absorbing foil removed, a balance for the two parts of the beam, each now at its unreduced intensity, I_0 , was obtained by altering the length of the lower part of the slit, S_2 , by means of a brass wedge, W . Finally, the foil was restored to its position, the discs set into rotation, and then their common opening adjusted until a balance was again indicated by the electrometer. Having attained this balance the discs were stopped and the common angular opening on each side read on a scale (described in the next section) and recorded as α .

If I is the intensity of the beam after passing through the foil then the ratio I/I_0 is obviously given by $2(\alpha)/360$ or $\alpha/180$. Since α and the mass of the foil per unit area were known, the value of the mass coefficient could be calculated directly, as is illustrated by the following typical example.

For a certain specimen of tin foil (No. 5) the value of α was found to be 81.6° . Hence $I/I_0 = 81.6/180 = e^{-(\frac{\mu}{\rho})M}$, where μ/ρ is the mass coefficient of absorption, and M is the mass of the foil per unit area, in this case 0.02486 gm./cm². By solving this equation the value of μ/ρ is found to be 31.8. The value of θ , the angle between the crystal plane and the X-ray beam, was observed to be $3^\circ 44'$. If a crystal spacing, d , of 2.814 Ångstrom units is assumed, the value of λ is found to be 0.3746 Å, from the Bragg relation $\lambda = 2d \sin \theta$.

From the above it is apparent that the experimental method and the calculations are both simple and direct. In applying the method to the problem undertaken, which will not be discussed in the present paper, one generally repeats several times, for any position of the chamber and of the crystal, the balance adjustments for the I_0 and the I beams alternately.

As the major improvements believed to have been developed during the course of the present work centre about the discs and the ionization chamber, further details concerning these parts as well as a discussion of their advantages will be included.

Sectored Discs

Since no description of rotating sectored discs suitable for the work at hand was found, a new type was developed. The structure of this apparatus is represented in Fig. 2. The discs, *E*, were made of cast lead, bounded by

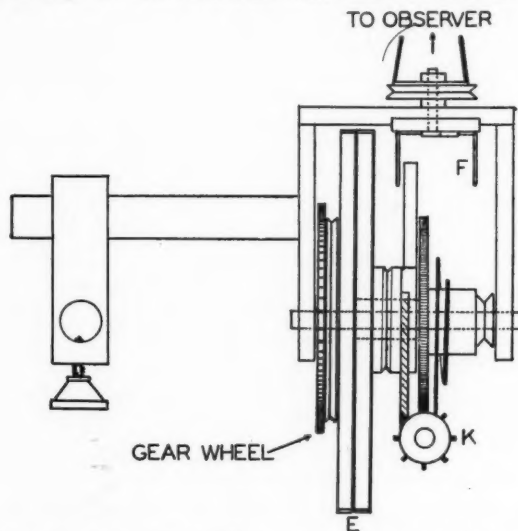


FIG. 2. The sectored discs. The capstan, *K*, can be turned either way by the fork, *F*, during the rotation of the discs. *F* is operated by means of a rod extending to the position of observer.

brass cylindrical walls, and each was turned on a lathe to a thickness of 4 mm., which is sufficient to stop all but about 0.001% of the most penetrating X-rays used in this work. Each disc has cut out of it a pair of 90° sectors, diametrically opposite to each other.

The brass rim of one of the discs carries a scale, while on the other is a pointer which indicates their common angular opening for a beam of radiation moving normally to the discs. The two discs can be rotated relatively to each other, without stopping them, by means of a worm and gear combination provided with a capstan wheel, *K*, on the worm head. When the capstan is turned the discs rotate relatively to each other, thereby increasing or decreasing their common aperture, depending on whether the sliding fork, *F*, is made to actuate the capstan on the one side or on the other. When the fork is in neutral position the capstan does not strike either of its prongs, and the opening remains constant.

Since the potential applied to the X-ray tube was obtained from a step-up transformer and mechanical rectifier combination, care had to be taken to avoid what may be called a stroboscopic effect in the X-rays passing through the rotating sectors, an effect pointed out by Becker and Warburton (1). Certain disc speeds were shown to be usable. One such speed was obtained and kept constant by rotating the discs by means of suitable gears turned by

a small synchronous motor of the phonic wheel type, rotating at 5 r.p.s., and driven by the same a-c. source that supplied the X-ray transformer. The sectors were thus rotated with constant speed which had a value of 1.912 r.p.s. By backing one of the gear wheels with a soft rubber washer, any chattering of the gears was prevented and smooth operation secured. With this arrangement the maximum possible error due to stroboscopic drift was calculated to be not greater than 0.5%, and it was considered to be much less for the speed of rotation used.

The discs and their motor were so mounted that they could be turned as a unit about the axis of the spectrometer, and be moved with the ionization chamber when its position was altered. The general validity of the sectored discs method was established by Becker and Warburton (1). This was checked further by the writers, as their experimentally obtained data showed a linear relation between sector openings and rates of deflection.

Incidentally, the same motor was used to drive the foil, which was in the form of a thin circular disc accurately cut between templates on a lathe and mounted to rotate in a plane perpendicular to the X-ray beam. Not only is it an easy matter to determine M accurately for such discs, but their rotation assures a true average effect on the intensity of the beam transmitted.

The Tri-Electrode Ionization Chamber

While the general scheme used in the work herein reported is similar to that of Stoner and Martin, several important modifications are involved. Their pair of semicylindrical ionization chambers is replaced by a single

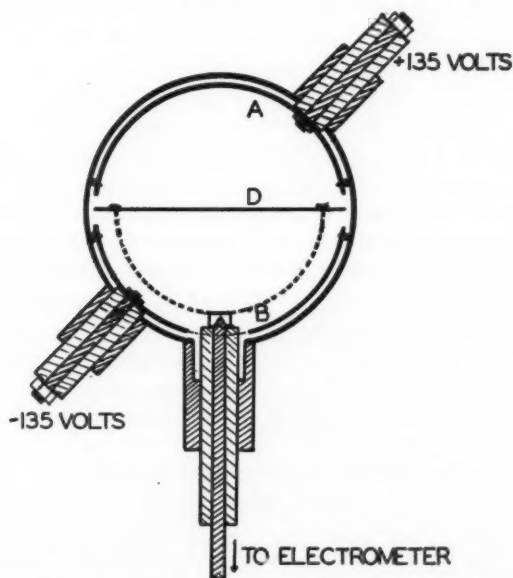


FIG. 3. Cross section view of the tri-electrode ionization chamber.

cylindrical brass case of which the middle cross section view is shown in Fig. 3. In this there are two large semicylindrical outer electrodes, *A* and *B*, placed opposite to each other, while in the median plane there is a flat electrode, *D*, which almost completely divides the chamber into two compartments, thus forming a tri-electrode chamber. *A* and *B* are maintained at potentials of +135 and -135 volts, respectively, by "B" batteries, while *D* is connected directly to one pair of quadrants of a Compton electrometer, the other pair of quadrants being grounded. *D* is supported by a single quartz insulator, while *A* and *B* are kept from touching the grounded brass case by quartz studs in their edges. The electrodes are made of aluminium sheet, and the case is made of brass tubing 2 in. in diameter. Quartz was found to be the only insulating material in common use that could be employed with continued success in the presence of the vapor of the ethyl bromide introduced to increase the absorption. The glass ethyl bromide bulb and the phosphorus pentoxide drying bulb are attached to the ionization chamber by conical ground glass-to-brass joints. The X-ray beams enter and leave the chamber through the thin aluminium foil windows.

The advantages of the balance method have already been outlined, but the tri-electrode ionization chamber described above provides certain improvements over the two chamber combination used by Wingårdh, or the variations employed by Stoner and Martin, among which the following may be mentioned.

(a) The two compartments of the chamber are at a minimum distance apart, and thus are affected to a lesser degree by outside radiations than in the case of either of the other two balance methods mentioned. That is, "natural" leak variations are reduced to a minimum. It follows that the balancing beams used have a minimum angle of divergence.

(b) Wingårdh having a double spectrometer, necessarily used two crystals and two spectrometer scales, etc., whereas the writers' tri-electrode ionization chamber made it possible, not only to use one scale system and a single crystal, but also to utilize the same region of the latter to a degree not possible even in Stoner and Martin's apparatus. The advantages thus obtained must be apparent to any one who has had to search for a really satisfactory crystal.

(c) Since the absorbing vapor used has direct access to all parts of the chamber, identical vapor conditions are assured in the two compartments of the chamber. This is felt to be a most important advantage since the ionization currents depend critically on the vapor pressures of the ethyl bromide. Structural conditions are also nearly identical in the compartments.

Further Discussion and Results

The method herein reported differs in one important element from that of Stoner and Martin. They used the sectorized discs only to calibrate an aluminium wedge which was subsequently used in their measurements, while the writers used the discs directly. It appeared that this extra step was

unnecessary and might introduce errors. In particular, it seems doubtful that a wedge calibrated under certain conditions would be equally reliable under other conditions involved in later investigations.

The possibility that the results obtained might depend, owing to scattering and fluorescent effects, on the exact locations of the sectors and the foil was considered. But a series of tests as to the effect of shifting positions, with a variety of wave-lengths, confirmed the finding of Woo (4) as to the improbability of errors due to any such variations within reasonable limits.

The curve shown in Fig. 4 is included as an indication of the character of the results obtainable with the experimental method described above. It represents the variation in the mass coefficient of absorption of silver through

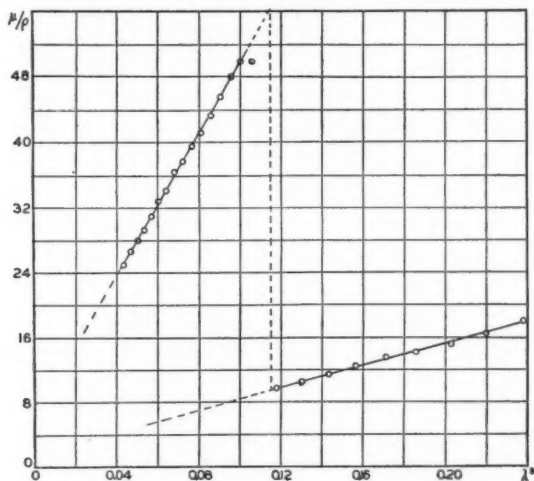


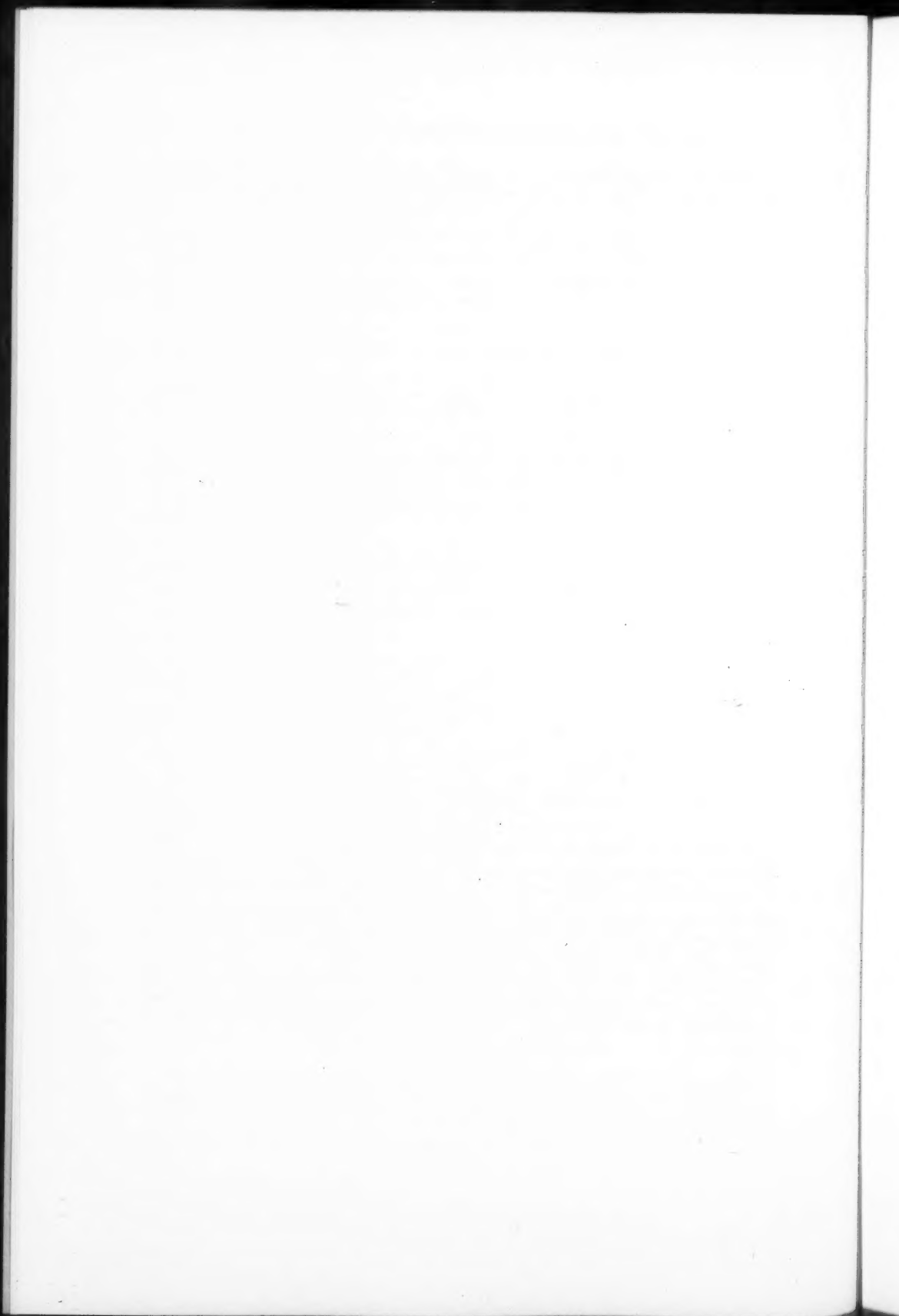
FIG. 4. Curve showing the relation between μ/ρ and λ^2 for silver in the region of the K discontinuity.

a range of wave-lengths extending through the region of the K limit of silver. The closeness with which the points fall on a straight line on either side of the K discontinuity is highly satisfactory. Incidentally, the fact that the curve obtained is linear, and that the absolute values of the mass coefficients of absorption and of the K discontinuity agree well with values obtained by others offer further support to the method developed.

It is believed that the general method described above might prove useful in various types of investigations involving the determination of absorption coefficients, as the application of the scheme is not limited to the study of metal foils.

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THE ALTERATION OF THE FLOW CHARACTERISTICS AND TEXTURE OF STARCH PASTES¹

BY WILFRED GALLAY²

Abstract

Starch pastes are classified according to the "length" of the flow or texture, and the practical importance of this characteristic in commercial applications for starch pastes is noted, *e.g.* for culinary uses. The differences in flow and texture may be attributed to the differences in phase-volume relations and the deformability of the swollen granules in the paste. It is shown that heating in water below the gelatinization point reduces both the volume occupied per unit concentration by the dispersed phase, and also increases the rigidity of the swollen granules. The viscosity of the paste is greatly reduced and the critical concentration of the starches is correspondingly increased by this treatment. The effect is particularly large in the case of potato starch, but is appreciable also with corn and wheat starches. Suspension of starches in dilute sulphurous acid (0.25% SO₂) effects a similar change in somewhat greater degree, hence it is probable that the flow characteristics of corn starch are altered during the process of extraction. The practical application of these modifications is briefly discussed.

When starches of different types are gelatinized or pasted in the same concentration, a wide variation in the properties of these pastes is obtained. These differences are highly important in the commercial utilization of starches, and in many instances it has been found empirically in industry that one type of starch yields pastes of the desired properties for a particular use only. The chief characteristic of a dilute paste is its viscosity, and it has been shown (1, 3, 4) that this property is governed by the volume relations between the dispersed and continuous phases and by the ease of deformation of the dispersed phase. By suitable acid-modification the phase-volume ratio and hence the viscosity of any starch may be varied over a wide range, the volume occupied by the granules decreasing continuously with increasing degree of modification. In more concentrated pastes which are still capable of flow, the paste is commonly classified as "long" or "short". If the paste is allowed to flow from a glass rod, a more or less continuous flow or a long streamer of paste denotes a "long" paste, whereas if the paste breaks off short, the term "short" paste is applied.

These differences are readily understandable on the basis of the physical picture of the dispersed phase in starch pastes. If the effective volume (1) of the starch is large and the dispersed phase is readily deformable, then a structure is set up which promotes more or less continuous flow of the granules

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past one another, and in which the flow is long because of the elasticity of the swollen granules. This is found to be the case in potato starch pastes and also to a great extent in pastes of cassava starch. In the case of corn or wheat starch, however, the pastes obtained are short. It has been shown (1) that the effective volume of corn starch is small compared with that of potato starch, and that the deformability or elasticity of the swollen granules is much less. In such a paste, it is obvious that there is a greatly lessened structure to hold the paste together in the case of free flow, as from a glass rod. The same considerations may be applied to still more concentrated pastes, which form a gel-like system, incapable of flow. These differ in so-called "texture" depending on the type of starch used. The texture may be long or short much as in the case of the free flow discussed above.

One example of the commercial importance of these differences might be mentioned specifically. One of the most important individual commercial applications for starch is in pastes for culinary purposes, *e.g.*, puddings. A corn starch paste of the proper concentration possesses the desired texture for this purpose. The paste is short so that no elastic resistance is offered to the edge of a spoon, and the paste breaks off cleanly when scooped out. A paste prepared from potato starch, however, even at much lower concentrations, shows great elasticity and the texture is long so that the table utensil carries away a streamer of paste when removed. The same factors, *i.e.*, elasticity and long texture, cause also a "tough" effect during mastication. A detailed discussion of various types of starch and their industrial uses will be given in a forthcoming publication (2).

The Effect of Moist Heat on the Paste-forming Characteristics of Starches

Acid modification of starches is generally carried out by heating a suspension of starch in dilute hydrochloric acid to 50° C. for a period depending on the degree of modification desired. During the course of experiments on acid modification in May, 1935, it was desired to ascertain the effect of the acid alone, and hence experiments were carried out to determine the effect of heating aqueous suspensions of starch below the gelatinization point.

There was no change in the appearance of the granules as a result of this treatment. When these heat-treated starches were pasted, however, microscopic observation showed that the swelling power of the granules, particularly in the case of potato starch, was greatly reduced compared to the swelling power of the untreated starch granules. The effect increased with time of treatment up to a maximum, after which further heat treatment appeared to have no effect. A semiquantitative measure of this decrease in the swelling power of the granules was obtained by pasting a dilute suspension of the starch under standard conditions, allowing it to settle, and measuring the minimum volume occupied by the paste. Table I shows a representative series of measurements on potato, corn and wheat starches. Check measurements were made in all cases.

It is noted that the effect of reduction in swelling power is very large in the case of potato starch. Dry heat alone (100° C.) for short periods had virtually no effect on the swelling power. A starch that had been treated with moist heat, filtered and dried, and retreated in water at 50° C. showed no further change in swelling power. Increase in temperature of treatment had the effect of a small increase in later paste volume. In addition to the decrease in effective volume after treatment in water at

50° C., there was also noted a decreased elasticity or deformability of the granules. The effect is apparently similar to that obtained after moderate acid modification.

The viscosities of pastes of various concentrations of these treated starches were measured in a MacMichael viscosimeter at 25° C. At higher concentrations, the pastes showed structural flow, according to the relation $F = KP^n$, where F is the flow, P is the pressure, K and n are constants. The critical concentration (1), above which structure was apparent, was found to be 1.4% for treated potato starch after maximum treatment. The critical concentration for untreated potato starch was found to be 0.45%. This showed the large decrease in volume occupied by the pasted granules due to the moist heat treatment. Similarly the critical concentration of treated corn starch was found to be 2.1–2.2%, as compared with the value 1.8% found for untreated corn starch. Furthermore, the increase in the exponent n with concentration c , i.e., dn/dc , was increased as a result of the moist heat treatment. This denoted a decrease in the deformability of the granules (1).

The greatly decreased effective volume of the pasted potato starch granules and the greater rigidity of these granules is immediately apparent in the greatly shortened texture of concentrated pastes. With reference again to the one specific commercial use mentioned, samples of this treated potato starch were submitted to two schools of domestic science for thorough test as to suitability in culinary products. Generally favorable reports were received. This showed that the pasting characteristics of the potato starch, and hence the paste texture, had been reasonably well adapted to this particular purpose. Since this work was done, another reference to the effect of warm water on the viscosity of dilute starch pastes has been noted (6).

TABLE I
EFFECT OF MOIST HEAT TREATMENT ON STARCHES

| Time of heating at 50° C., hr. | Minimum volume (cc.) occupied by 1 gm. of heat-treated starch after pasting | | |
|--------------------------------|---|------|-------|
| | Potato | Corn | Wheat |
| 0 | 44.1 | 21.0 | 15.8 |
| 0 | 45.7 | 20.0 | 15.5 |
| 1 | 28.8 | 18.8 | 12.9 |
| 1 | 28.5 | 20.0 | 12.9 |
| 3.5 | 24.1 | 19.8 | 13.1 |
| 3.5 | 24.7 | 19.5 | 13.6 |
| 5.0 | 25.5 | 19.8 | 12.6 |
| 5.0 | 25.0 | 19.7 | 12.3 |
| 8.0 | 23.9 | 18.0 | 12.1 |
| 8.0 | 25.6 | 17.6 | 12.1 |

The Effect of Dilute Sulphurous Acid Modification on Starches

The corn grain consists of a hard outer husk, a starchy endosperm and the embryo or germ. In order to remove the last-named, the first step in the process of corn starch extraction is the softening of the grain by steeping it in water containing a small amount of sulphurous acid, at an elevated temperature. Generally a solution containing about 0.25–0.3% of sulphur dioxide is used at a temperature of about 50° C. for an extended period. The time of steeping varies from 36 hr. to 4 days. This is followed by removal of the germ and subsequent separation and purification of the starch. The steeping procedure is entirely lacking in the extraction of potato starch, which is essentially a removal of the starch by sieving, flotation, centrifuging and similar means.

It was considered of interest therefore to determine the effect of dilute sulphurous acid on potato starch. The starch was suspended in 0.27% sulphur dioxide solution at 50° C. for five hours. Microscopic observation on pastes of this starch showed that the swelling power of the granules was greatly decreased by this treatment. The critical concentration of this starch was measured in the manner previously described (1), and found to be 1.7%, compared with 0.45% and 1.8% for untreated potato and corn starches respectively. The pastes obtained with this acid-steeped starch were short in texture and resembled those of corn starch very closely. This showed that the elasticity of the original potato starch granules (after pasting) had been greatly reduced.

Potato starch, pretreated with sulphur dioxide solution in the above manner, was then acid-modified by suspending it in 2.05% hydrochloric acid at 50° C. Samples were withdrawn at regular intervals and the viscosities of their pastes determined in a MacMichael viscosimeter at 25° C., at 3% concentration. All the pastes showed structural flow throughout and the data were well expressed by $M = KR^{\frac{1}{n}}$, where M is the deflection of the inner

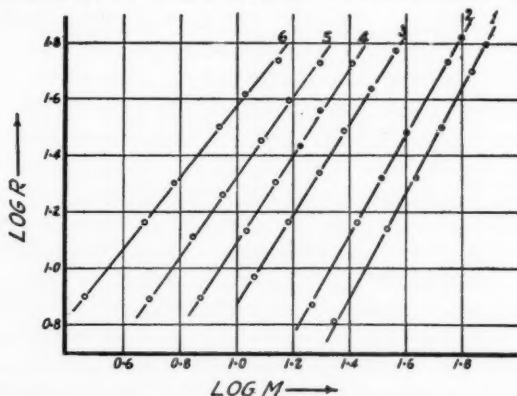


FIG. 1. Flow-pressure relations on a logarithmic scale, in a series of acid-modified potato starches prepared from a starch that was pretreated with dilute sulphur dioxide solution. Curves numbered in order of increasing degree of modification. Concentration, 3%.

cylinder in degrees MacMichael, R is the rate of rotation of the outer cylinder in r.p.m., and K and n are constants. Fig. I shows, on a logarithmic scale, the results obtained. Table II shows the values obtained for the exponent n in this series, compared with corresponding results obtained on a series of acid-modified starches prepared in the same manner from untreated potato starch.

As previously noted (3), the experimental error in these measurements is of the order of ± 0.03 in the value of n . It is noted from Table II that the rate of modification is distinctly increased during the early stages, after

which the differences become small. No immediately comparable series of acid-modified corn starches is available, but by interpolation and comparison with results previously shown for corn starches, it is seen that the rate of modification of the potato starch treated with sulphur dioxide does not approach that of corn starch.

Commercial Application

It has been shown (1, 3, 4) that the viscosity and texture of starch pastes are dependent largely on the phase-volume relation in the paste and on the rigidity of the swollen granules. By the slight treatments noted above, these properties of various starches may be altered. It is quite probable, also, that the paste-forming characteristics of a starch are altered during the process of extraction, as in the case of corn starch. It has been noted during the course of this work that appreciable differences in paste-forming characteristics are obtained in corn starches from different extraction plants. Undoubtedly this is at least partly due to a variation in the extraction procedure. In the case of potato starch, it has been noted (7) that a large variation in paste viscosity is obtained, depending on the hardness of the water used in the purification of the starch after extraction. The moist heat treatment described above can be readily incorporated in the extraction of potato starch, if a product which will yield a paste of shorter texture is desired. It is to be emphasized that starches in general are comparatively readily adaptable from this point of view, and that an understanding of the physical characteristics of a starch required for a particular use must be obtained prior to attempts at adaptation.

Experimental

The moist heat treatment was carried out by heating a suspension of starch in water, approximately 22° Bé., in a thermostat at 50° C. Samples were withdrawn at the stated intervals, filtered and dried at 50° C. Sulphur

TABLE II
EFFECT OF SULPHUR DIOXIDE PRETREATMENT ON ACID
MODIFICATION

| Time of modification, min. | n | |
|----------------------------------|-----------------------------|------------------------------|
| | Potato starch, untreated | Potato starch, pretreated |
| 40 | 2.31 | 1.88 |
| 80 | 1.90 | 1.81 |
| 120 | 1.75 | 1.63 |
| 160 | 1.58 | 1.59 |
| 200 | 1.38 | 1.46 |
| 240 | 1.34 | 1.26 |

dioxide pretreatment was carried out in a similar manner, with the addition of 0.27% of sulphur dioxide to the suspension water. The samples removed were thoroughly washed, and dried at 50° C. The swelling power of the starches was measured as follows (5): 1 gm. of starch was suspended in 5 cc. of cold water and gelatinized by the addition of 50 cc. of water at 95° C. from a pipette in a standard way without agitation. The paste was maintained in a thermostat at 80° C. for 15 min. and then poured into a graduated flask containing 45 cc. of water at room temperature. After it had stood until the paste occupied a minimum volume, the latter was noted. Viscosities of pastes were measured in a MacMichael viscosimeter as previously described (3).

Acknowledgments

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LII. THE PREPARATION, SEPARATION AND IDENTIFICATION OF THE ISOMERIC PROPYLIDENE, ISOBUTYLIDENE, *t*-AMYLIDENE AND DIBROMOETHYLIDENE GLYCEROLS AND THE GENERAL PROPERTIES OF GLYCEROL CYCLIC ACETALS¹

BY SAUL M. TRISTER² AND HAROLD HIBBERT³

Abstract

The condensation of propionaldehyde, isobutyraldehyde, trimethylacetaldehyde and dibromoacetaldehyde with glycerol has been carried out in the presence of a catalyst (40% sulphuric acid) at 90° C., and the resulting products have been shown to consist in each case of a mixture of the five- and six-membered cyclic acetals. The separation of these isomers from the acetal mixture was rendered possible by the difference in the physical properties of their benzoates. The structure of the latter was proved by saponification, methylation, hydrolysis and isolation of the resulting glycerol α - and glycerol β -methyl ethers respectively.

With the isomers from dibromoacetaldehyde this method could not be used, owing to the labile character of the bromine atoms in presence of alkali. Their structures were proved by direct synthesis of the five-membered acetal benzoate from glycerol α -benzoate and dibromoacetaldehyde.

The data obtained provide additional evidence of the marked influence exerted by the polar character of the aldehyde on the extent and character of acetal condensation. Increase in the electronegative character increases the amount formed of the five-membered acetal and decreases that of the six-membered. Trimethylacetaldehyde condensed readily with glycerol in absence of a catalyst. Lowering of temperature, in presence of the catalyst, favored the formation of the six-membered acetals, in agreement with the earlier work of van Roon. The results further confirm the Hibbert-Michael Ring Partition Principle.

A general comparison is made of the physical properties of the ethylidene-, propylidene-, isobutylidene-, *t*-amylidene-, bromoethylidene-, and dibromoethylidene glycerol acetals.

By substituting diphenylamine for aniline in the synthesis of trimethylacetaldehyde from trimethylpyruvic acid the yield is increased from 25 to 40%.

Introduction

In view of the ease of formation of both five- and six-membered cyclic acetals, in general, as shown by the various partition experiments carried out by Hibbert and co-workers (5-10, 12, 13) during the last twelve years, it was concluded that in the condensation between glycerol and any aldehyde, a "ring partition" takes place to give a reaction product consisting of a mixture of five- and six-membered cyclic acetals.

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It was of interest to ascertain how far this "Hibbert-Michael Ring Partition Principle" is influenced by the polar character of the aldehyde, the nature of the catalyst and time and temperature of reaction.

The results of this investigation indicate that the proportion in which the isomeric glycerol cyclic acetals are formed depends on two factors: (a) the relative amounts of half-acetals formed by interaction with the α -

and β -hydroxyl groups of the glycerol molecule, and (b) tendency and ease of ring formation as influenced by spatial conditions such as polar character of the reacting aldehydes. As the polar character of the carbonyl group becomes more negative, the ease of addition of the aldehyde to the polyhydroxy compound increases as does also the stability of the resulting half-acetal, so that the relative ease of ring formation should decrease and this is found to be the case (Table I).

It is evident from Table I that the relative proportion in which the five- and six-membered cyclic acetals are formed is influenced markedly by the polar character of the aldehyde.

This finds further support in the fact that condensation

TABLE I
PROPORTION OF ISOMERIC ALKYLIDENE GLYCEROL
ACETALS FORMED FROM VARIOUS
ALIPHATIC ALDEHYDES
Catalyst, sulphuric acid (40%);
temperature of reaction, 90° C.

| Aldehyde | Yield of mixed cyclic acetals, % | Ratio of 5- to 6-membered isomer |
|--|----------------------------------|----------------------------------|
| $\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \text{C}-\text{CHO}$ | 80 | 3 : 2 |
| $\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \text{CH}-\text{CHO}$ | 80 | 3 : 1 |
| $\text{CH}_3\text{CH}_2\text{CHO}$ | 80 | 4 : 1 |
| CH_3CHO (12) | 63 | 4 : 1 |
| CH_2BrCHO (6) | 57* | 15 : 1 |
| CHBr_2CHO | 40 | 15 : 1 |
| CCl_3CHO (9) | 20 | No 6-membered isomer |

* The condensation of bromoacetaldehyde was first carried out by E. Hallonquist (6). He obtained the isomeric cyclic acetals (yield, 37%), using crude bromoparacetaldehyde. Repetition of this work employing the pure crystalline tribromoparacetaldehyde (20) gave a yield of 57%.

of acetone (8) and of trimethylacetaldehyde (16) with glycerol takes place in the absence of a catalyst, while with chloral (9), dibromoacetaldehyde, acetaldehyde (12) and isobutyraldehyde, cyclic acetal formation takes place only under the influence of an acid catalyst (sulphuric acid, zinc chloride, etc.) From this behavior it may be concluded that in the absence of a catalyst no reaction is likely to take place with propionaldehyde or with monobromoacetaldehyde.

While the proportion of the six-membered acetal formed in the case of *t*-amylidene glycerol is relatively high, it may be seen (Table I) that increase in the negative polar character of the aldehyde brings about a gradual decrease in the amount of six-membered acetal formation from trimethylacetaldehyde to acetaldehyde, followed by a large decrease until chloral is reached at which point no detectable six-membered cyclic acetal formation occurs.

Effect of Temperature and Influence of Catalyst on Cyclic Acetal Conversion

Van Roon (21) was the first to point out the important role played by temperature on the ratio of isomeric acetals formed in the condensation of an aldehyde with glycerol. Using benzaldehyde and glycerol, he found that at a temperature above 150° C. virtually no six-membered isomer is obtained when cyclic acetal formation is brought about by the presence of a small quantity (generally about 1% by weight) of anhydrous hydrogen chloride, and that the amount increases with lowering of temperature. By maintaining the mixture of isomeric benzylidene cyclic acetals at 0° C. for 48 hr., the five-membered derivative undergoes transformation into the six-membered. The results of similar investigations carried out by the writers using propylidene-, isobutylidene-, bromoethylidene- (6) and dibromoethylidene glycerols in presence of anhydrous hydrogen chloride (1% by weight) are summarized in Table II. The products were heated for the periods specified, then cooled

TABLE II
EFFECT OF TEMPERATURE ON RATIO OF ISOMERIC CYCLIC ACETAL FORMATION
Catalyst, 1% (by weight) of anhydrous hydrogen chloride

| Time of heating, hr. | Temp. °C. | Ratio of five-membered to six-membered cyclic acetals | | | |
|--|-----------|---|--------------------------------|--|------------------------------------|
| | | Propylidene glycerol acetals | Isobutylidene glycerol acetals | Monobromoethylidene glycerol acetals (6) | Dibromoethylidene glycerol acetals |
| 1 | 150 | Decomposes 70 : 1 | Approx. 100% 5-membered | | 11 : 1 |
| 1 | 100 | | | | |
| 1 | 50 | 6 : 1 | | | 8 : 1 |
| 1 | 25 | 4 : 1 | | | 8 : 1 |
| 48 | 25 | 2 : 1 | Approx. 1 : 9 | 7 : 1 | 8 : 1 |
| 48 | 0 | | | | 8 : 1 |
| Condensation carried out by the customary technique at 90° C., with 40% sulphuric acid as catalyst 15 : 1 15 : 1 | | | | | |

to room temperature, benzoylated, and the relative amounts of the two isomers present determined. While accuracy greater than 2-3% cannot be claimed for these determinations, this does not affect the general character of the conclusions drawn from the data.

Presumably in all these cases, ring fission occurs under the influence of the catalyst, and the reaction then proceeds in the direction of the equilibrium ring formation, as conditioned by the temperature employed.

Whereas ring fission was found to occur in an acid medium, it was definitely proved that none occurs in an alkaline medium.

Experimental

Preparation THE ISOMERIC PROPYLIDENE GLYCEROL ACETALS

Freshly distilled glycerol (242 gm.) and sulphuric acid (40%; 42 drops) were slowly heated on a water bath with vigorous stirring. Propionaldehyde (140 gm.) was added and the mixture kept at 90° C. for five hours. It was then cooled, extracted with ether, and the solution dried (potassium carbonate). The ether was distilled off and the residual oil fractionated; yield, 260 gm. (80%) of mixed acetals, b.p. 80–90° C./10 mm.

Benzoylation

Benzoyl chloride (134 gm.), dissolved in dry pyridine (135 gm.), was added slowly to a solution of the crude mixed acetals (126 gm.) in dry pyridine (133 gm.), the temperature being kept at –5 to –10° C. The mixture was allowed to stand overnight at 40° C. It was then slowly poured with vigorous stirring into a litre of cold distilled water. A yellow oil separated out which was extracted with ether. The ether solution was washed with 3% sulphuric acid then with 5% sodium carbonate, and finally with water. After drying (sodium sulphate), the ether was removed, the residual oil heated to 100° C./15 mm. and maintained at that temperature for two hours in order to remove all traces of pyridine. Yield of crude benzoylated acetals, 170 gm. (76%). This crude mixture was dissolved in ligroin (b.p. 80–90° C.), seeded with a crystal of 1,3-propylidene glycerol acetal 2-benzoate (obtained in preliminary experiments) and kept for 24 hr. at 0° C. A thick paste was obtained, and the crystals were separated from the adhering oil by stirring the pasty, crystalline mixture with warm ligroin (b.p. 60–70° C.). A relatively good separation was obtained in this manner because of the greater solubility of the oil, as compared with the solid, in warm ligroin. The crystals were filtered off and dissolved in hot ligroin. On cooling, the product crystallized in rhombic plates. The bulk of the ligroin was then evaporated and the ligroin-oil mixture re-seeded at 0° C. This procedure was repeated several times until no further separation took place. Yield of the six-membered isomer, m.p. 74–75° C., 27 gm. Found: C, 65.7, 65.4; H, 6.9, 6.8%. Calcd. for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8%. The ligroin was removed and the residual oil fractionated. This yielded 1,2-propylidene glycerol acetal 3-benzoate; b.p. 147–149° C./1 mm.; n_D^{25} , 1.5078; d_4^{25} , 1.1249. Yield, 107 gm. Found, C, 65.9; H, 6.8%. Calcd. for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8%. Total combined yield of pure benzoates, 60%. Ratio of the five- to the six-membered acetal, 4 : 1.

Hydrolysis of 1,2-Propylidene Glycerol 3-Benzoate

The benzoate (100 gm.) was heated with a mixture of 10% sodium hydroxide (420 cc.) and 95% ethyl alcohol (25 cc.) to 50° C. on a water bath, and the mixture shaken for two hours. A clear homogeneous solution was formed. Potassium carbonate (350 gm.) was added and the mixture extracted with ether. The precipitated sodium benzoate was filtered off, and the aqueous layer and sodium benzoate were then extracted several times with ether. Fractionation of the residue from the combined ether solutions yielded

1,2-propylidene glycerol acetal; b.p. 70–72° C./3 mm.; n_D^{25} , 1.4424; d_4^{25} , 1.0767. Yield, 33 gm. (60%). Found: C, 53.8; H, 9.1%. Calcd. for $C_6H_{12}O_3$: C, 54.5; H, 9.1%.

Hydrolysis of 1, 3-Propylidene Glycerol 2-Benzate

The benzoate (21.7 gm.) was hydrolyzed by the method used in the preceding experiment. In this case, however, 24 hr. continuous shaking was required to obtain a homogeneous solution. After extraction, distillation yielded 1,3-propylidene glycerol; b.p. 50–51° C./2 mm.; n_D^{25} , 1.4448, d_4^{25} , 1.0889. Yield, 6.6 gm. (60%). Found: C, 54.0; H, 9.1%. Calcd. for $C_6H_{12}O_3$: C, 54.5; H, 9.1%.

Methylation of 1,2-Propylidene Glycerol Acetal

This acetal (15 gm.) was methylated with dimethyl sulphate (27 gm.) and 30% sodium hydroxide (63 cc.). The methylating agents were allowed to drop from separate tap-funnels into the acetal, and the mixture was stirred vigorously (temperature, 40–50° C.). The reaction mixture was kept slightly alkaline throughout the addition, which required three hours. On completion of the addition, the temperature of the water-bath was raised to 70° C. and maintained there for two hours. The contents of the flask was cooled by immersion in ice-water, and the cold, alkaline solution extracted five times with ether. After extraction, distillation yielded 1,2-propylidene glycerol 3-methyl ether; b.p. 67–69° C./17 mm.; n_D^{25} , 1.4221, d_4^{25} , 1.0001. Yield, 9.1 gm. (55.2%). Found: C, 57.2; H, 9.3%. Calcd. for $C_7H_{14}O_3$: C, 57.5; H, 9.6%.

Methylation of 1,3-Propylidene Glycerol Acetal

In the methylation of this compound the Purdie methylation technique (18) gave higher yields than the Haworth process (4) used in the preceding experiment.

To 1,3-propylidene glycerol acetal (9 gm.) was added dry silver oxide (40 gm.) and methyl iodide (80 gm.) over a period of five hours at 46–47° C. Chloroform (50 cc.) was then added, and the mixture stirred for 15 min. at 50° C. It was cooled, filtered, and the silver oxide extracted four times with boiling chloroform. Fractional distillation of the residue from the combined chloroform extracts yielded 1,3-propylidene glycerol 2-methyl ether; b.p. 89–90° C./23 mm.; n_D^{25} , 1.4335; d_4^{25} , 1.0237. Yield, 6.9 gm. (75%). Found: C, 57.1; H, 9.0%. Calcd. for $C_7H_{14}O_3$: C, 57.5; H, 9.6%.

Hydrolysis of 1,2-Propylidene Glycerol Acetal 3-Methyl Ether

The method used was that of Irvine, McDonald and Soutar (14). The ether (5 gm.) was dissolved in an equal volume of water and concentrated hydrochloric acid (six drops) added. On refluxing for 10 min. at the boiling-point, liberation of propionaldehyde began, and after further refluxing for 30 min. the solution was allowed to simmer for two to three hours in a small Erlenmeyer flask until gas evolution ceased. Water was added to replace that lost by evaporation. The hot solution was then neutralized with solid

lead carbonate, cooled, filtered, and subjected to vacuum distillation. This yielded glycerol α -methyl ether; b.p. 110° C./13 mm.; n_D^{17} , 1.4463; d_4^{17} , 1.1198. Yield, 1 gm. (30%).

Hydrolysis of 1, 3-Propylidene Glycerol Acetal 2-Methyl Ether

This ether was hydrolyzed in the manner described in the preceding paragraph, similar quantities being used. Fractional distillation under reduced pressure yielded glycerol β -methyl ether; b.p. 120 – 121° C./13 mm.; n_D^{17} , 1.4505; d_4^{17} , 1.1306. Yield, 1.5 gm. (45%).

Preparation

THE ISOBUTYLIDENE GLYCEROL ACETALS

Isobutyraldehyde (20 gm.) was condensed with glycerol (50.4 gm.), dilute sulphuric acid (6 drops) being used as catalyst, by the method described for the preparation of propylidene glycerol. Yield of isomeric acetals, b.p. 102 – 108° C./12–15 mm., 32 gm. (80%).

Benzoylation

The isomeric acetals (157 gm.) were benzoylated by the method outlined above for propylidene glycerol benzoates, benzoyl chloride (142.7 gm.) and pyridine (285 gm.) being used. Yield of six-membered isomer, m.p. 73.5° C., 50 gm. Found: C, 67.3; H, 7.2%. Calcd. for $C_{14}H_{18}O_4$: C, 67.2; H, 7.2%. Fractionation of the residual oil gave five-membered isomer; b.p. 159 – 162° C./5 mm.; n_D^{25} , 1.5041; d_4^{25} , 1.0695. Yield, 140 gm. Found: C, 67.5; H, 7.3%. Calcd. for $C_{14}H_{18}O_4$: C, 67.2; H, 7.2%. Total yield of pure benzoates, 75%. Ratio of five-membered to six-membered acetals, 3 : 1 (approximately).

Hydrolysis of the Isobutylidene Glycerol Acetal Benzoates

Hydrolysis of the five-membered benzoate (10 gm.) in the usual manner, with 10% sodium hydroxide (42 cc.) and ethyl alcohol (2 cc.), gave a 1,2-isobutylidene glycerol acetal; b.p. 69 – 72° C./2 mm.; n_D^{25} , 1.4428; d_4^{25} , 1.0456. Yield, 3.5 gm. (60%). Found: C, 57.1; H, 9.3%. Calcd. for $C_7H_{14}O_3$: C, 57.5; H, 9.6%. Similarly, the six-membered benzoate (10 gm.) gave 1,3-isobutylidene glycerol acetal, b.p. 55 – 56° C./2 mm. Yield, 2.9 gm. (50%). The oil thus obtained solidified immediately, and the product was recrystallized from warm ligroin (b.p. 30 – 50° C.) as small needle-like crystals, m.p. 38 – 39° C. Found: C, 58.0; H, 9.3%. Calcd. for $C_7H_{14}O_3$: C, 57.5; H, 9.6%.

1,2-Isobutylidene Glycerol Acetal 3-Methyl Ether

Methylation of 1,2-isobutylidene glycerol acetal (10 gm.) with methyl iodide (100 gm.) and silver oxide (50 gm.) gave 1,2-isobutylidene glycerol 3-methyl ether; b.p. 70 – 71° C./15 mm.; n_D^{25} , 1.4246; d_4^{25} , 0.9677. Yield, 7 gm. (65%). Found: C, 59.5; H, 9.8%. Calcd. for $C_8H_{16}O_3$: C, 60.0; H, 10.0%.

1,3-Isobutylidene Glycerol Acetal 2-Methyl Ether

1,3-Isobutylidene glycerol (8 gm.) was methylated using methyl iodide (80 gm.) and silver oxide (40 gm.). This gave 1,3-isobutylidene glycerol acetal 2-methyl ether; b.p. 80–81° C./15 mm.; n_D^{25} , 1.4393; d_4^{25} , 0.9971. Yield, 6 gm. (72.5%). Found: C, 59.4; H, 9.7%. Calcd. for $C_8H_{16}O_3$: C, 60.0; H, 10.0%.

Hydrolysis of the Isomeric Ethers

The five-membered ether (5 gm.) gave glycerol α -methyl ether, b.p. 110° C./13 mm.; yield, 1.7 gm. (50%). The six-membered isomer (5 gm.), gave glycerol β -methyl ether; b.p. 120–121° C./13 mm.; yield, 2.0 gm. (60%).

Attempted Condensation of Isobutyraldehyde and Glycerol in Absence of a Catalyst

Freshly distilled glycerol (12.6 gm.) was heated at 90° C. for 24 hr. with vigorous stirring, allowed to cool and then extracted with ether. The oil recovered from the ether was unchanged isobutyraldehyde, while the ether-insoluble portion was unchanged glycerol. This indicated that no condensation had occurred.

THE AMYLIDENE GLYCEROL ACETALS*

Preparation of Trimethylacetaldehyde

Trimethylacetaldehyde was prepared from pinacone hydrate. This was converted into pinacolone (11) which was then oxidized to trimethyl pyruvic acid (19). The latter was converted into trimethylacetaldehyde (maximum yield, 25%) by the use of aniline (19). Substitution of diphenylamine for aniline increased the yield to 40%. The following procedure, using diphenylamine, was adopted.

Trimethyl pyruvic acid (28 gm.) and recrystallized diphenylamine (12 gm.) were placed in a three-necked flask, fitted with a stirrer, thermometer, and condenser, so that the aldehyde could distil over as rapidly as formed. The mixture was heated (oil bath), with vigorous stirring, to 150–200° C. and maintained there until no further trimethylacetaldehyde distilled over. Presumably two reactions take place simultaneously, since both carbon dioxide and water are liberated in the reaction: (a) formation of the diphenylamine salt which decomposes into the aldehyde, carbon dioxide and diphenylamine; and (b) condensation of two moles of diphenylamine with the carbonyl group of the pyruvic acid. The crude trimethylacetaldehyde was dried (sodium sulphate), filtered, and fractionated. Yield; 6.5 gm. (40%), b.p. 74–78° C. Further study of the function of the diphenylamine in this reaction might lead to a much higher yield.

Condensation of Trimethylacetaldehyde with Glycols and Glycerol in Absence of a Catalyst

Preliminary experiments carried out by heating together equimolecular quantities of glycerol and trimethylacetaldehyde for 15–24 hr. at 50° C. in absence of a catalyst gave yields of the mixed acetals (b.p. 102–108° C./20 mm.) as high as 60% of the theoretical value.

* This work was carried out in co-operation with Arthur Paquet (16).

Similar results were obtained with ethylene glycol and propylene glycol (1 : 3).

1,2-t-Amylidene Glycol—Colorless liquid, pleasant odor; b.p. 129–130° C./760 mm.; d_{4}^{20} , 0.9189; n_D^{20} , 1.4147. Yield, 54%. Found: C, 64.9; H, 10.8%. Theoretical: C, 64.6; H, 10.8%. Mol. wt. (ethylene dibromide); 132.1, 129.3. Theoretical, 130.1.

1,3-t-Amylidene Glycol—B.p. 148° C./760 mm. Yield, 46%.

Preparation and Benzoylation of the Isomeric t-Amylidene Glycerol Acetals

Trimethylacetaldehyde (20 gm.) was condensed at 90° C. with glycerol (21.4 gm.), 40% sulphuric acid (3 drops) being used as catalyst. Time of reaction, three hours. Yield of crude isomeric acetals, b.p. 90–100° C./10 mm., 24.8 gm. (75%) (increased later to 80% by use of a purer sample of the aldehyde).

The acetal mixture (25 gm.) was treated with benzoyl chloride (21.9 gm.) in pyridine solution at 0° C., and the acetals were isolated. Ratio of five- to six-membered acetals, 3 : 2.

The 1,3-*t*-amylidene glycerol acetal benzoate crystallized from ligroin (b.p. 60–70° C.) in small needle-like crystals, m.p. 93.5° C. Yield, 4 gm. Found: C, 67.9; H, 7.6%. Calcd. for $C_{16}H_{20}O_4$: C, 68.2; H, 7.6%.

The 1,2-*t*-amylidene glycerol acetal benzoate was fractionated under reduced pressure; b.p. 169° C./8 mm.; n_D^{25} , 1.4998; d_4^{25} , 1.0850. Yield, 6 gm. Found: C, 67.7; H, 7.3%. Calcd. for $C_{16}H_{20}O_4$: C, 68.2; H, 7.6%.

Hydrolysis of the Isomeric t-Amylidene Glycerol Benzoates

The 1,2-*t*-amylidene glycerol 3-benzoate (10 gm.) was hydrolyzed with 10% sodium hydroxide (42 cc.) and 95% ethyl alcohol (2 cc.). This yielded the 1,2-*t*-amylidene glycerol acetal; b.p. 83–84° C./6 mm.; n_D^{25} , 1.4431; d_4^{25} , 1.0168. Yield, 3.4 gm. (57%). Found: C, 59.2; H, 9.8%. Calcd. for $C_9H_{16}O_3$: C, 60.0; H, 10.0%.

1,3-*t*-Amylidene glycerol 2-benzoate gave, similarly, 1,3-*t*-amylidene glycerol acetal. From ligroin it crystallized in small clusters of needle-like crystals, m.p. 45° C. Yield, 56%. Found: C, 59.5; H, 10.3%. Calcd. for $C_9H_{16}O_3$: C, 60.0; H, 10.0%.

Methylation of the Isomeric t-Amylidene Glycerol Acetals

Treatment of 1,2-*t*-amylidene glycerol acetal (2.5 gm.) with methyl iodide (25 gm.) and silver oxide (15 gm.) yielded the methyl ether; b.p. 66–68° C./6 mm.; n_D^{25} , 1.4278; d_4^{25} , 0.9655. Yield, 2.1 gm. (75%). Found: C, 61.6; H, 10.0%. Calcd. for $C_9H_{18}O_3$: C, 62.1, H, 10.3%.

The 1,3-*t*-amylidene glycerol 3-methyl ether was prepared in a similar manner; b.p. 79–81° C./6 mm.; n_D^{25} , 1.4401; d_4^{25} , 0.9947. Yield, 85%. Found: C, 61.5; H, 10.2%. Calcd. for $C_9H_{18}O_3$: C, 62.1; H, 10.3%.

Hydrolysis of the t-Amylidene Glycerol Methyl Ethers

The 1,2-*t*-amylidene glycerol 3-methyl ether (2 gm.) was hydrolyzed with concentrated hydrochloric acid (3 drops). This yielded glycerol α -methyl ether; b.p. 110° C./13 mm.; n_D^{17} , 1.4463. Yield, 0.6 gm. (50%). Similarly 1,3-*t*-amylidene glycerol 2-methyl ether gave glycerol β -methyl ether; b.p. 120° C./13 mm.; n_D^{17} , 1.4505. Yield, 50%.

THE DIBROMOETHYLIDENE GLYCEROL ACETALS

Preparation of Dibromoacetaldehyde

Three methods for the preparation of dibromoacetaldehyde were tried. (a) Dworzack's method (1) required much time and gave a poor yield (about 15%); (b) Pinner's method (17) required less time and gave a somewhat better yield (25%); (c) Mylo's method (15) was found to be the simplest and gave the best results. It was therefore adopted, with certain modifications.

Paracetaldehyde (44 gm.) was mixed with chloroform (40 cc.) in a three-necked flask fitted with a mercury seal stirrer, a U-bent capillary dropping-funnel and a glass tube through which the hydrobromic acid, evolved during the reaction, was allowed to pass into two safety bottles, the first empty and the second half-filled with water. The chloroform solution was cooled in an ice bath and freshly distilled bromine (320 gm.) slowly added, with vigorous stirring, at 0° C. to -5° C. over a period of three hours. The temperature of the mixture was then allowed to rise slowly to about 75° C. over a further period of three hours and maintained at this point until no further hydrobromic acid was evolved, stirring being continued throughout. The reddish oily product was at once submitted to fractional distillation at ordinary pressure. If this is not carried out *immediately*, considerable decomposition occurs when the mixture is heated to 100° C. Yield of crude dibromoacetaldehyde (b.p. 133-140° C./761.7 mm.), 103 gm. (51.5%). Refractionation yielded 83 gm. (42%) of pure dibromoacetaldehyde; b.p. 136-137.5° C./761.7 mm.

Preparation and Benzoylation of the Isomeric Dibromoethylidene Glycerol Acetals

Dibromoacetaldehyde (50 gm.) was condensed with glycerol (30 gm.) in presence of 40% sulphuric acid. Yield of isomeric dibromoethylidene glycerols, b.p. 128-138° C./3 mm., 28 gm. (40%). This mixture was treated with pyridine (30 gm.) and benzoyl chloride (14 gm.). Yield of crude isomeric benzoates, 29 gm. (70%). When left at room temperature for several days the product began to crystallize slowly to a thick paste.

By spreading the paste on a porous plate, the oil was absorbed after some ten days and the solid six-membered acetal left almost free from the liquid five-membered isomer. The solid benzoate was then scraped off and dissolved in hot ligroin-benzene mixture (1 : 1). On cooling, the six-membered acetal crystallized in small needle-like crystals, m.p. 67.5°. Yield, 1.3 gm. Found: Br, 42.4, 42.1%. Calcd. for $C_{12}H_{12}O_4Br_2$: Br, 42.1%.

The oil absorbed by the porous plate was extracted with ether, mixed with the ligroin solution left from the crystallization of the six-membered acetal, the solvents were removed and the residual oil was again inoculated with the

crystalline isomer. This was repeated until no further separation occurred. The residual oil was fractionally distilled. This yielded pure 1,2-dibromoethylidene glycerol 3-benzoate; b.p. 167–171° C./3 mm.; n_D^{25} , 1.5608; d_4^{25} , 1.6597. Yield: 19.5 gm. Found: Br, 41.5, 42.1%. Calcd. for $C_{12}H_{12}O_4Br_2$: Br, 42.1%.

The ratio of the yields of solid six-membered benzoate to the liquid five-membered benzoate was approximately 1:15.

Determination of Structure of the Isomeric Dibromoethylidene Glycerol Acetals

Proof of structure of the dibromoethylidene glycerol acetals was not possible by the customary procedure of hydrolysis on account of the labile character of the bromine atoms in presence of alkali. The problem was solved by carrying out a direct synthesis of the five-membered acetal by condensing glycerol α -benzoate with dibromoacetaldehyde. The product was found to be identical with the liquid benzoate isolated from the benzoylated mixture of the dibromoethylidene glycerol acetals. It follows that the corresponding crystalline isomer must possess the six-membered structure.

Synthesis of 1,2-Dibromoethylidene Glycerol 3-Benzoate from Glycerol α -Benzoate and Dibromoacetaldehyde

Glycerol α -benzoate was prepared by the method of Fischer and Bergmann (2) as modified by Hallonquist (3).

A mixture of dibromoacetaldehyde (25 gm.), glycerol α -benzoate (25 gm.) and 40% sulphuric acid (10 drops) was heated at 110–120° C. for 10 hr., allowed to stand at 40° C. for a further 48 hr., cooled, and poured slowly, with vigorous stirring, into water (500 cc.). The resulting oil was decanted and washed several times with water, then extracted with ether, and the five-membered acetal isolated in the usual manner; b.p. 167–169° C./4 mm.; n_D^{27} , 1.5565; d_4^{25} , 1.6590. Yield, 14 gm. (30%). The physical properties are in good agreement with those of the pure five-membered benzoate; b.p. 167–171° C./3 mm.; n_D^{25} , 1.5608; d_4^{25} , 1.6597.

The results serve to confirm the identity of the two products and thus to establish the structure of both isomeric acetals.

Hydrolysis of 1,2-Dibromoethylidene Glycerol 3-Benzoate

This benzoate was hydrolyzed with 10% sodium hydroxide and ethyl alcohol in the usual manner. It was necessary to shake the mixture continually for 48 hr. before a clear homogeneous solution was obtained. The acetal was isolated in the usual manner; b.p. 124–127° C./3 mm.; n_D^{25} , 1.5423; d_4^{25} , 1.8742. Yield, 43%. Found: Br, 57.5; 57.6%. Calcd. for $C_8H_8O_3Br_2$: Br, 57.8%.

Hydrolysis of 1,3-Dibromoethylidene Glycerol 2-Benzoate

The hydrolysis of this compound (which required 70 hr.) gave 1,3-dibromoethylidene glycerol; b.p. 117–119° C./3 mm.; n_D^{25} , 1.5457; d_4^{25} , 2.0251. Yield, 23%. Found: Br, 57.7; 57.4%. Calcd. for $C_8H_8O_3Br_2$: Br, 57.8%.

General Properties of the Glycerol Cyclic Acetals

Based on the numerous investigations by Hibbert and co-workers (6, 12), the following generalizations may be drawn from Table III.

TABLE III
PHYSICAL PROPERTIES OF THE ALKYLIDENE GLYCEROL CYCLIC ACETALS

| Compound | B.p., °C. | M.p., °C. | n_D^{17} | n_D^{25} | d_4^{17} | d_4^{25} |
|---|----------------|--------------|------------|------------|------------|------------|
| 1,2-Ethylidene glycerol (12) | 68-70/2 mm. | | 1.4413 | | 1.1243 | |
| 1,3-Ethylidene glycerol (12) | 52/2 mm. | | 1.4532 | | 1.1477 | |
| 1,2-Ethylidene glycerol 3-benzoate (12) | 144-145/2 mm. | | 1.5145 | | 1.1618 | |
| 1,3-Ethylidene glycerol 2-benzoate (12) | | 86 | | | | |
| 1,2-Ethylidene glycerol 3-methyl ether (12) | 56-58/23 mm. | | 1.4177 | | 1.0224 | |
| 1,3-Ethylidene glycerol 2-methyl ether (12) | 80/23 mm. | | 1.4375 | | 1.0705 | |
| 1,2-Propylidene glycerol | 70-72/3 mm. | | | 1.4424 | | 1.0767 |
| 1,3-Propylidene glycerol | 50-51/2 mm. | | | 1.4448 | | 1.0889 |
| 1,2-Propylidene glycerol 3-benzoate | 147-149/1 mm. | | | 1.5078 | | 1.1249 |
| 1,3-Propylidene glycerol 2-benzoate | | 74-75 | | | | |
| 1,2-Propylidene glycerol 3-methyl ether | 67-69/17 mm. | | | 1.4221 | | 1.0001 |
| 1,3-Propylidene glycerol 2-methyl ether | 89-90/23 mm. | | | 1.4335 | | 1.0237 |
| 1,2- <i>i</i> -Butylidene glycerol | 69-72/2 mm. | | | 1.4428 | | 1.0456 |
| 1,3- <i>i</i> -Butylidene glycerol | 55-56/2 mm. | 38-39 | | | | |
| 1,2- <i>i</i> -Butylidene glycerol 3-benzoate | 159-162/5 mm. | | | 1.5041 | | 1.0695 |
| 1,3- <i>i</i> -Butylidene glycerol 2-benzoate | | 73.5 | | | | |
| 1,2- <i>i</i> -Butylidene glycerol 3-methyl ether | 70-71/15 mm. | | | 1.4246 | | 0.9677 |
| 1,3- <i>i</i> -Butylidene glycerol 2-methyl ether | 80-81/15 mm. | | | 1.4393 | | 0.9971 |
| 1,2- <i>t</i> -Amylidene glycerol | 83-84/6 mm. | | | 1.4431 | | 1.0168 |
| 1,3- <i>t</i> -Amylidene glycerol | | 45 | | | | |
| 1,2- <i>t</i> -Amylidene glycerol 3-benzoate | 169/8 mm. | | | 1.4998 | | 1.0850 |
| 1,3- <i>t</i> -Amylidene glycerol 2-benzoate | | 93.5 | | | | |
| 1,2- <i>t</i> -Amylidene glycerol 3-methyl ether | 66-68/6 mm. | | | 1.4278 | | 0.9655 |
| 1,3- <i>t</i> -Amylidene glycerol 2-methyl ether | 79-81/6 mm. | | | 1.4401 | | 0.9947 |
| 1,2-Bromoethylidene glycerol (6) | 150-151/23 mm. | | | 1.5008 | | 1.6437 |
| 1,3-Bromoethylidene glycerol (6) | 144-145/22 mm. | | | 1.5067 | | 1.6557 |
| 1,2-Bromoethylidene glycerol 3-benzoate (6) | 170/0.6 mm. | | | 1.5452 | | 1.4618 |
| 1,3-Bromoethylidene glycerol 2-benzoate (6) | | 109 | | | | |
| 1,2-Bromoethylidene glycerol 3-methyl ether (6) | 117-119/22 mm. | | | 1.4720 | | 1.4694 |
| 1,3-Bromoethylidene glycerol 2-methyl ether (6) | 128-129/21 mm. | | | 1.4790 | | 1.4973 |
| 1,2-Dibromoethylidene glycerol | 124-127/3 mm. | | | 1.5423 | | 1.8742 |
| 1,3-Dibromoethylidene glycerol | 117-119/3 mm. | | | 1.5457 | | 2.0251 |
| 1,2-Dibromoethylidene glycerol 3-benzoate | 167-171/3 mm. | | | 1.5608 | | 1.6597 |
| 1,3-Dibromoethylidene glycerol 2-benzoate | | 67.5 | | | | |

1. The boiling points of the isomeric 1,2- (five-membered) and 1,3- (six-membered) glycerol cyclic acetals lie within a narrow range. Their separation from a mixture is thus rendered very difficult, if not impossible. Separation, however, can readily be effected indirectly, by converting the acetals into their corresponding benzoates and taking advantage of the differences in solubility of the latter in ligroin. In all cases the six-membered acetal has

a lower boiling point, higher refractive index and higher density than the five-membered. All the five-membered acetals are liquids at room temperature, as are also the six-membered with the exception of the isobutylidene and *t*-amylidene glycerol acetals, which are crystalline solids.

2. The benzoates of the five-membered acetals are all liquids at room temperature, while the corresponding benzoates of the six-membered isomer are, without exception, solids.

3. The boiling points, refractive indices and densities of the five-membered acetal derivatives of the monomethyl ethers of the ethylidene, propylidene, isobutylidene, and *t*-amylidene glycerols are lower than those of the corresponding six-membered isomers.

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MICROCHEMICAL TECHNIQUE

I. SOME INNOVATIONS IN THE MICROMETHOXYL AND MICROCARBON-HYDROGEN DETERMINATION¹

BY E. V. WHITE² AND GEORGE F. WRIGHT³

Abstract

A new flowmeter and preheater for the Friedrich carbon-hydrogen determination are described. The micromethoxyl apparatus as described by Pregl has been simplified, only one absorption tube being necessary.

Introduction

Because the widespread use of microchemical technique is comparatively recent, and, indeed, is decidedly in the developmental stage, the writers consider it worth while to report, from time to time, such variations in apparatus and method as they have found to be improvements on the known procedures. It is their hope that other contributors to this journal will likewise appreciate the importance of frequent reports in a branch of chemistry that has not yet developed beyond the manipulative stage.

The writers consider that, for the research chemist who performs carbon-hydrogen determinations occasionally rather than continuously, the method of Friedrich (1) is the most satisfactory. Although the introduction of a flowmeter, obviating the continuous use of a Mariotte bottle, is one of the most valuable features of this apparatus, the flowmeter itself is very troublesome because of the stopcock which varies the orifice of the instrument. This stopcock is difficult to adjust, and, when adjustment is finally attained, the wax used to secure it is so subject to temperature and atmospheric change that the calibration is utterly unreliable from day to day. Thus the obvious advantage of an adjustable orifice over a fixed orifice has been curtailed by the undependable stopcock.

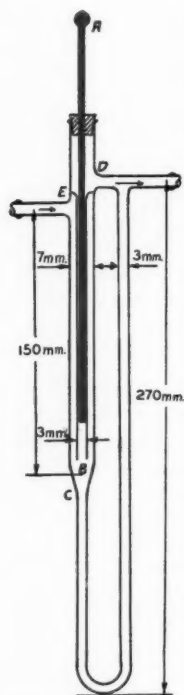
This fault has been obviated in the flowmeter shown in Fig. 1 because a relatively large movement of the plunger *A* in the tube *BE* causes only a small variation in the height of the manometer liquid. For the same reason the instrument retains its calibration adjustment. Such an adjustment is convenient because it enables one to measure gas flow in terms of discrete scale units. The construction is simple, requiring a single ring seal, *E*, but the tube *BE*, which is of the same size as the manometer (about 3 mm.), should be carefully selected so that it fits as closely around the plunger *A* as is possible without sticking at any point. The concentric space between *A* and *BE* constitutes the orifice of the instrument. The seals at *C* and *D* should be offset so that the back of the manometer is coplanar with the back of the large jacket around the orifice; when so constructed, a scale lies smoothly

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FIG. 1. *The flowmeter.*

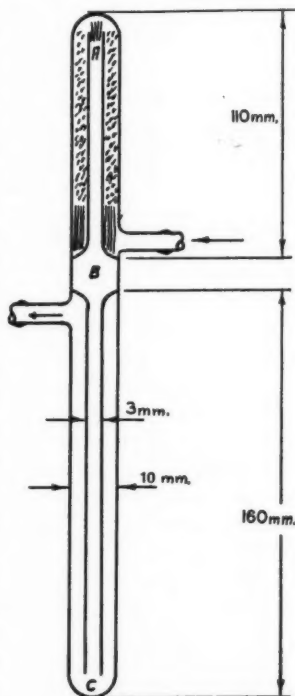
behind the apparatus. The plunger slides smoothly in the rubber stopper at the top of the device when it is lubricated from above with a small amount of glycerol. When the flowmeter is properly constructed there is no trouble in measuring a flow of 4 cc. per min. within the limits of 0.1 cc., and its utility is apparent in the fact that by replacing the plunger in an apparatus of this type with a smaller plunger we are measuring rates as high as 200 cc. per min. in our ozonizer.

For use with corrosive gases the plunger *A* can be sealed to the upper part of the jacket after approximate calibration has been obtained, thus disposing of the rubber stopper.

A number of so-called preheaters, for burning combustible substances in a gas stream have been described (1, 3). The writers' only claim for the device described here (Fig. 2) is simplicity of construction, an attribute to be considered in this case since the life of a preheater is not long. The apparatus is constructed from 10 mm. Pyrex tubing, into which two 4-mm. tubes, *AB* and *BC*, are joined by ring seals at *B*. The gas inlet and outlet being attached, the bottom of the tube is sealed off, and, in operation, may be immersed in a beaker of water to cool the burned gases (1).

Into the annulus around *BA* is packed 1.5 cm. lengths of coarse fibre asbestos, and then, fluffy platinized asbestos. The top of *BA* is then loosely packed with coarse fibre asbestos and the top of the 10 mm. tube is sealed off. An electrical heating unit surrounds the top of the preheater. It should not fit too tightly and should be closed at the top with a stopper of asbestos paper which can be removed in order that the correct (dull red) temperature may be ascertained.

The writers have adopted, in large part, the recommendations of Gibson and Caulfield (2) in the use of the Vieböck (5, 6) modification of the micromethoxyl determination, and find that the largest error, the action of light on the bromine solutions, is eliminated by the use of a blank on the absorbing bromine-potassium bromide solution. Such a blank, however, when manipu-

FIG. 2. *The preheater.*

lated so as to simulate the conditions of the determination is clumsy to handle with the double absorbing tube recommended by Pregl (4). By the writers' procedure the freshly prepared aqueous bromine-potassium bromide solution is exactly divided between the two receivers which are immediately immersed in the ice bath, as shown in Fig. 3. Before the outlet tube from the methoxyl apparatus is inserted into one of these receivers, a glass sleeve, *h*, is held at *i*; when the assembly is complete the sleeve *h* is allowed to fall so that it rests on the constriction of the receiver, as shown. This sleeve, about 1.5 cm. long, is cut from glass tubing about 1 mm. larger than the tube forming the bottom of the receivers, and is notched four times around the periphery of the edges with a wet file. When the sleeve is correctly made it permits free circulation between the top and bottom of the receiver (tested by allowing a drop of permanganate solution to run down the side of the receiver with bubbles of gas rising), and yet it will retain the ascending bubble of gas long enough to facilitate absorption. Tufts of cotton placed in the mouths of the receivers further insure complete retention of the evolved methyl iodide.

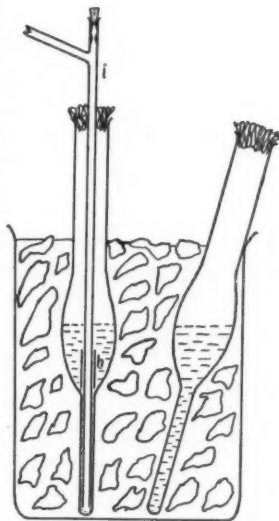


FIG. 3. The ice bath.

Acknowledgments

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THE KINETICS OF COUNTERCURRENT ABSORPTION TOWERS¹BY H. G. LITTLER²

Abstract

The kinetics of countercurrent towers absorbing a gas which obeys Henry's law have been worked out by a more rigid method than that used by Donnan and Masson (2). An equation is obtained which, unlike the Donnan and Masson formula, is the expression of a process which is thermodynamically irreversible. This is in accordance with the requirements of thermodynamics. The theoretical variation of the concentration of the soluble gas in the two phases throughout the tower is examined by means of the new equation.

The first attempt to deduce an expression for the kinetics of countercurrent absorption towers in which the solute gas obeyed Henry's law was made by Donnan and Masson (2).

The expression they obtained was

$$\text{Log}_e \frac{\{(k-f)M_1 + (fM_2 - N_1)\}}{kM_2 - N_1} = \frac{k_1 k_2 S(k-f)}{V_0} h.$$

It can be shown that this equation is an expression for a process which can, in the limit, be made thermodynamically reversible. This can be demonstrated as follows. The above equation is obtained by using a modified form of an expression deduced by Adeney and Becker (1), namely:

$$\frac{dw}{dt} = k_2(km - n),$$

where dw is the weight of soluble gas transferred through a unit area of interface from the gaseous to the liquid phase in time dt , k is Henry's coefficient, m and n are the concentrations of the soluble gas in the gaseous and liquid phases respectively, and k_2 is a constant called by Donnan and Masson the "dissolution coefficient". Donnan and Masson assumed that this equation of Adeney and Becker held at all points in the absorption tower, *i.e.*, for any element of gas-liquid interfacial area dA .

Now it is clear that the function $(km - n)$ can be considered as a potential or driving force whose magnitude governs the rate and direction of the transfer of the soluble gas. Denote this function by π . If π is positive, soluble gas will be transferred from the gaseous to the liquid phase, the liquid being unsaturated with respect to the gas; if π is negative, the liquid is supersaturated with respect to the soluble gas, and gas will be transferred from the liquid to the gas phase; if $\pi = 0$, no net transfer of soluble gas will take place, the liquid being saturated with respect to the soluble gas, and the system is, therefore, in equilibrium.

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If the value of this function at the bottom of the tower is denoted by π_1 , at the top of the tower by π_2 , and at any point in the tower by π , then the Donnan and Masson equation can be written

$$\text{Log}_e \frac{\{kM_1 - fM_1 + fM_2 - N_1\}}{\pi_2} = \frac{k_1 k_2 S(k - f)}{V_g} h,$$

but $fM_2 - N_1 = fM_1 - N_2$ (from Donnan and Masson's Equation (1) (2, p. 237)) and $k_1 Sh = \text{total area of gas-liquid interface} = A_T$.

Hence the equation becomes

$$\begin{aligned} \text{Log}_e \frac{\pi_1}{\pi_2} &= k_2 \left(\frac{k}{V_g} - \frac{1}{V_L} \right) A_T \\ \pi_2 &= \pi_1 e^{k_2 \left(\frac{1}{V_L} - \frac{k}{V_g} \right) A_T}, \end{aligned}$$

or for any point in the tower the equation is

$$\pi = \pi_1 e^{k_2 \left(\frac{1}{V_L} - \frac{h}{V_g} \right) A}.$$

When the rates of flow are so adjusted that $\frac{1}{V_L} = \frac{k}{V_g}$, then $\pi = \pi_1$, that is, all points in the tower are at the same degree of equilibrium. Under these conditions, therefore, as π_1 is decreased the tower as a whole can be made to approach progressively nearer to equilibrium, and in the limit the process can be made thermodynamically reversible.

This result is fully in accordance with that obtained by Van Arsdell (3) who showed that the Donnan and Masson equation led, for the mean driving force in the tower, to a formula similar to that employed for heat transfer. It is well known that such a process can be made, in the limit, reversible.

It can be shown from thermodynamic reasoning that the process of countercurrent absorption is irreversible, and it is therefore not possible so to adjust the conditions in the tower as to approach without limit equilibrium at all points. This is a point of some interest and is worth further study. It is true that many workers have modified the Donnan and Masson equation, but these modifications have all had for their object the formulation of expressions which would apply to more complex cases than the simple one considered by Donnan and Masson. Such modifications are, of course, of great importance from the practical point of view where what is primarily required is an equation that can be used in the design of countercurrent absorption towers that are to be used in practical work.

In spite, however of its remoteness from industrial practice, the simple case of the absorption of a gas obeying Henry's law in a countercurrent tower operating under the simple conditions assumed by Donnan and Masson has a considerable theoretical importance. This is in part due to the fact that the simple case lends itself readily to easy mathematical and thermodynamic treatment, and partly because in studying countercurrent absorption freed from the many complexities introduced somewhat arbitrarily by the necessities of industrial practice, it is probable that a clearer insight may be obtained of the essential nature of the countercurrent operation itself.

The origin of the discrepancy between the Donnan and Masson equation and the conclusions of thermodynamics must be sought for in the assumptions made by Donnan and Masson in deducing their expression. An examination of these assumptions shows that only one of them is theoretically inadmissible, namely, the assumption that the volume of gas remains constant throughout a tower which is operating at constant pressure. In other parts of the analysis it is tacitly assumed that the gases obey the gas laws as, for example, when partial pressures are converted to concentrations and generally where concepts involving the simple kinetic theory are introduced. Now it is theoretically clearly inadmissible that a mixture of gases which are assumed to obey the gas laws for one purpose shall be considered, for another purpose, as remaining at constant volume and constant pressure during a process which removes a portion of one component from the gaseous mixture. Obviously either the pressure must fall or the volume decrease. This was pointed out by Donnan and Masson in their paper, but they assumed the constancy of the gas volume in order to simplify the mathematical treatment, and they were careful to state that the analysis made in this way would apply only to cases where the soluble gas concentration was small. It will be shown later that this is not the only condition necessary to justify the use of the Donnan and Masson equation.

It is reasonable to suppose, therefore, that if this assumption be dropped, an equation will be obtained which is theoretically consistent and will fulfil the thermodynamic requirement that the countercurrent process is an irreversible one.

Consideration of the Kinetics of Countercurrent Towers

An analysis is given below by which the simple case of countercurrent absorption considered by Donnan and Masson is treated without making the assumption that the gas volume remains constant throughout the tower. All the other assumptions made by Donnan and Masson are retained and the following symbols are used.

- C = the concentration of the soluble gas in moles per unit V of gas or liquid.
- λ = $\frac{\text{equilibrium concentration of soluble gas in liquid phase}}{\text{equilibrium concentration of soluble gas in gaseous phase}}$
= the solubility coefficient, and, as the gas obeys Henry's law, λ is constant at constant temperature.
- t = time.
- n = number of moles of soluble gas in either liquid or gas phase that pass any diameter of the tower in unit time.
- N = number of moles of insoluble gas in gas phase that pass any diameter of the tower in unit time.
- P , R and T have their usual significance of pressure, gas constant and absolute temperature.

V = the total volume of gas which passes any diameter of the tower in unit time.

w = the weight of soluble gas in grams transferred from one phase to the other in a given time.

W = the weight of soluble gas in grams transferred from one phase to the other in unit time.

K_2 = the Donnan and Masson "dissolution coefficient" in terms of moles and is assumed constant throughout the tower.

V_L = volume of liquor injected into the tower in unit time.

A_T = total gas and liquid interface; A , the interface measured upwards to any point. Since the tower is supposed to be of constant diameter and uniformly packed, $A = h\pi r^2 S$, where h is the height of any point measured upward from the bottom of the tower, r is the radius of the tower and S the interfacial area per unit volume of packing. Since S and r are constant, $A \propto h$.

g refers to gas, L refers to liquid, 1 refers to the base of the tower, 2 to the top.

Thus C_g is concentration of soluble gas in the gas phase at any point in the tower, and C_{g1} the concentration in the gas phase at the base of the tower.

Consider, again, Adeney and Becker's equation in the modified form given by Donnan and Masson,

$$\frac{dw}{dt} = k_2(km - n),$$

where dw is the weight of gas in grams transferred through a unit area of interface from gas to liquid in time dt . For an area A and with the above symbols the equation becomes.

$$\frac{dw}{dt} = k_2(\lambda C_g - C_L)A. \quad (1)$$

This equation applies to any process of absorption of a gas obeying Henry's law in which the concentrations remain constant over the finite area A . In a countercurrent absorption tower this condition is not satisfied, since the concentrations of the soluble gas in both liquid and gas phases change continuously from point to point. The equation will, therefore, apply only over an element of the interface dA , and differentiating with respect to A we obtain,

$$\frac{d^2w}{dt dA} = k_2(\lambda C_g - C_L),$$

or,

$$w = \iint k_2(\lambda C_g - C_L) dt dA + \text{constant}, \quad (2)$$

the solution of which, if the integration be taken over the whole countercurrent tower, should give the expression required. The integration with respect to t is obtained by considering the tower after it has reached a steady

state in which the gas and liquor rates are constant. In these circumstances neither C_g nor C_L is a function of t so that the equation becomes

$$w = \int k_2(\lambda C_g - C_L)t \, dA + \text{constant.} \quad (3)$$

The integration constant obtained from this integration must equal zero, since when $t = 0$, $w = 0$.

The equation may be further simplified by putting $t = 1$ when $w = W$, the weight of gas transferred in unit time. Rearranging we obtain

$$A = \int \frac{dW}{k_2(\lambda C_g - C_L)} + \text{constant.} \quad (4)$$

Now dW , the weight of gas transferred in unit time, is proportional to the number of moles of solute gas lost from the gas phase in unit time, *i.e.*, $dW \propto -dn_g$; therefore, the equation may be written

$$AK_2 = \int \frac{-dn_g}{\lambda C_g - C_L} + \text{constant.} \quad (5)$$

If we consider a section of the tower below any diameter we know, if the tower be gas- and liquor-tight, that

$$\begin{aligned} n_{g1} + n_L &= n_g + n_{L1}, \\ \text{therefore } n_L &= n_g - (n_{g1} - n_{L1}), \end{aligned}$$

and putting $(n_{g1} - n_{L1}) = \Delta$, a constant throughout the tower, we have

$$n_L = n_g - \Delta. \quad (6)$$

Now since the gases obey the gas laws we know that

$$PV = (n_g + N)RT \quad (7)$$

and from definition

$$\lambda C_g - C_L = \lambda \frac{n_g}{V} - \frac{n_L}{V_L} \quad (8)$$

Substituting Equations (6) and (7) in Equation (8) we obtain

$$\lambda C_g - C_L = \frac{n_g^2 - \left(\frac{V_L P \lambda}{RT} + \Delta - N \right) n_g - N \Delta}{-V_L(N + n_g)}, \quad (9)$$

and Equation (5) becomes

$$AK_2 = \int \frac{V_L(N + n_g)dn_g}{n_g^2 - \left(\frac{V_L P \lambda}{RT} + \Delta - N \right) n_g - N \Delta} + \text{constant.} \quad (10)$$

Since Δ may be positive or negative, the solution of Equation (10), in general, takes three forms according as

$$\left(\frac{V_L P \lambda}{RT} + \Delta - N \right)^2 \begin{matrix} \geq \\ > \end{matrix} \left| 4N\Delta \right|.$$

It can be shown that the first condition, namely,

$$\left(\frac{V_L P \lambda}{RT} + \Delta - N\right)^2 = |4N\Delta|$$

is physically impossible, because if it is possible then Equation (9) may be written

$$\lambda C_g - C_L = \frac{(n_g - \alpha)^2}{-V_L(N + n_g)},$$

where α is the root of the quadratic. It follows therefore that for all real values of n_g , $\lambda C_g - C_L$ is negative. This means, physically, that the liquor is supersaturated with respect to the soluble gas throughout the length of the tower. This condition is impossible for an absorption tower.

It can also be shown that if Δ be negative the condition

$$\left(\frac{V_L P \lambda}{RT} - \Delta - N\right)^2 < |4N\Delta|$$

is impossible because in these circumstances the numerator of the fraction in Equation (9) can be written,

$$\begin{aligned} n_g^2 - \left(\frac{V_L P \lambda}{RT} - \Delta - N\right)n_g + N\Delta &= \left[n_g - \frac{1}{2}\left(\frac{V_L P \lambda}{RT} - \Delta - N\right)\right]^2 \\ &+ \frac{4N\Delta - \left(\frac{V_L P \lambda}{RT} - \Delta - N\right)^2}{4}. \end{aligned} \quad (11)$$

Now from the above condition it follows that $4N\Delta - \left(\frac{V_L P \lambda}{RT} - \Delta - N\right)^2$ is positive, therefore the left-hand side of Equation (11) must be positive and $\lambda C_g - C_L$ must be negative for all real values of n_g . We are left then with the two possible conditions,

$$\left(\frac{V_L P \lambda}{RT} + \Delta - N\right)^2 < |4N\Delta| \quad \text{when } \Delta \text{ is positive}$$

and

$$\left(\frac{V_L P \lambda}{RT} + \Delta - N\right)^2 > |4N\Delta| \quad \text{when } \Delta \text{ is positive or negative.}$$

Both these conditions lead to an identical solution of Equation (10), namely:

$$AK_2 = V_L \left[\frac{N+\alpha}{\alpha-\beta} \log_e (n_g - \alpha) + \frac{N+\beta}{\beta-\alpha} \log_e (n_g - \beta) \right] + \text{constant}, \quad (12)$$

where

$$\alpha = \frac{\left(\frac{V_L P \lambda}{RT} + \Delta - N\right) - \sqrt{\left(\frac{V_L P \lambda}{RT} + \Delta - N\right)^2 + 4N\Delta}}{2},$$

and

$$\beta = \frac{\left(\frac{V_L P \lambda}{RT} + \Delta - N\right) + \sqrt{\left(\frac{V_L P \lambda}{RT} + \Delta - N\right)^2 + 4N\Delta}}{2}.$$

Now when $n_g = n_{g1}$, $A = 0$, and when $n_g = n_{g2}$, $A = A_T$. Therefore,

$$K_2 = \frac{V_L}{A_T(\alpha - \beta)} \left[(N + \alpha) \log_e \frac{n_{g2} - \alpha}{n_{g1} - \alpha} - (N + \beta) \log_e \frac{n_{g2} - \beta}{n_{g1} - \beta} \right]. \quad (13)$$

This expression should represent the kinetics of countercurrent absorption for the simple case considered by Donnan and Masson, and, since no assumption has been made as to the constancy of the gas volume, the equation should fulfil the thermodynamic requirement that countercurrent towers cannot be made to approach equilibrium without limit at all points throughout their length.

The Irreversibility of the Process

That this equation represents an irreversible process can be shown as follows: upon differentiation we obtain

$$-dn_g = K_2 \frac{n_g^2 - \left(\frac{V_L P \lambda}{RT} + \Delta - N \right) n_g - N \Delta}{-V_L(N + n_g)} dA. \quad (14)$$

Now at equilibrium $-dn_g = 0$, and this condition will be fulfilled only when

$$n_g^2 - \left(\frac{V_L P \lambda}{RT} + \Delta - N \right) n_g - N \Delta = 0, \quad (15)$$

but this will be possible only when n_g has a value equal to one of the two roots of this equation, and, therefore, since a quadratic has two and only two roots, equilibrium can be reached in the tower at only two points, all other parts being at some distance removed from equilibrium. That is to say, the tower cannot be brought into equilibrium as a whole and the process is therefore irreversible. The two equilibrium points occur when $n_g = \alpha$ or β . These points, if they exist at all, must be at the top and bottom of the tower, as the following examination shows.

Position of the Equilibrium Points

Three cases arise according as to whether

$$\Delta \begin{matrix} > \\ = \\ < \end{matrix} 0$$

Case 1 Δ positive

In this case the discriminant of the roots of Equation (15) is greater than

$$\left(\frac{V_L P \lambda}{RT} + \Delta - N \right)^2,$$

so that α is negative and β is positive. Such towers, therefore, can have only one point of equilibrium in them, because n_g can never equal α , since a negative number of moles is physically meaningless.

Now in any absorption tower

$$n_{g1} > n_g > n_{g2},$$

and writing Equation (9) in the form

$$\lambda C_g - C_L = \frac{(n_g - \alpha)(n_g - \beta)}{-V_L(N + n_g)},$$

we see that when

$$\begin{aligned} n_g < \beta & \quad \lambda C_g > C_L \\ n_g = \beta & \quad \lambda C_g = C_L \\ n_g > \beta & \quad \lambda C_g < C_L. \end{aligned}$$

The last condition is physically impossible in an absorption tower, so that if equilibrium is to exist at all it must be when

$$n_{g1} = \beta,$$

and the equilibrium point is therefore at the base of the tower.

Case 2 $\Delta = 0$

In this case Equation (9) may be written

$$\lambda C_g - C_L = \frac{n_g \left[n_g - \left(\frac{V_L P \lambda}{RT} - N \right) \right]}{-V_L(N + n_g)}, \quad (16)$$

when

$$\lambda C_g = C_L, \quad n_g = \frac{V_L P \lambda}{RT} - N. \quad (17)$$

Therefore there is only one equilibrium point possible between the liquor and the gas.

Since, when $\lambda C_g > C_L$, n_g must be $< \frac{V_L P \lambda}{RT} - N$ throughout the length of the tower, the equilibrium point if it exists at all must be at the base of the tower.

Case 3 Δ negative

Two cases arise according as

$$(a) \quad \frac{V_L P \lambda}{RT} < \Delta + N$$

or,

$$(b) \quad \frac{V_L P \lambda}{RT} > \Delta + N.$$

When Δ is negative the discriminant of the roots of Equation (15) is less than $\left(\frac{V_L P \lambda}{RT} - \Delta - N \right)^2$, therefore both roots will have the same sign and will be negative in Case (a) and positive in case (b).

In Case (a), therefore, equilibrium is impossible in the tower. In Case (b) we may write Equation (9) in the form

$$\lambda C_g - C_L = \frac{(n_g - \alpha)(n_g - \beta)}{-V_L(N + n_g)}. \quad (18)$$

Now, inspection of the roots shows that $\beta > \alpha$, so that we see that $C_g - C_L$ is negative when $n_g > \beta$ or $< \alpha$. Therefore $\beta \geq n_g \geq \alpha$.

Hence the two points, if they exist at all, must be at the top and bottom of the tower.

Substitution of any of these equilibrium values in Equation (13) shows that when equilibrium is attained at any point $A_T = \infty$. Hence as the interfacial area of an absorption tower is made progressively greater, other conditions being equal, there is a tendency for equilibrium to be approached at either one or two points, depending on conditions. These equilibrium points are situated at the top and bottom of the tower and cannot occur at any other point.

The Mean Driving Force in a Tower

A concept frequently employed in the literature is the "mean driving force" or "mean absorption head" of an absorption tower. Van Arsdel (3) showed that on the basis of the Donnan and Masson formula this worked out to be:

$$\text{Mean driving force} = \frac{(KM_1 - N_2) - (KM_2 - N_1)}{\log_e \frac{KM_1 - N_2}{KM_2 - N_1}}.$$

By using Equation (13) the formula obtained is as follows,

amount of gas transferred in unit time = $K_2 \times \text{area} \times \text{mean driving force}$.

Now the amount of gas transferred in unit time is $(n_{g1} - n_{g2})$, therefore

$$\text{M.D.F.} = \frac{(n_{g1} - n_{g2})(\alpha - \beta)}{V_L \left[(N + \alpha) \log_e \frac{n_{g2} - \alpha}{n_{g1} - \alpha} - (N + \beta) \log_e \frac{n_{g2} - \beta}{n_{g1} - \beta} \right]}. \quad (19)$$

Values of Adeney and Becker's Function, $\lambda C_g - C_L$, Throughout the Tower

The values of the function $\lambda C_g - C_L$ at different points in the tower throw some light on the working of absorption towers.

Calling $\lambda C_g - C_L$, π as before, Equation (9) can be put in the form,

$$\pi = \frac{n_g^2 - \left(\frac{V_L P \lambda}{RT} + \Delta - N \right) n_g - N \Delta}{-V_L (N + n_g)}.$$

On differentiation,

$$\frac{d\pi}{dn_g} = \frac{P \lambda N}{RT(N + n_g)^2} - \frac{1}{V_L}. \quad (20)$$

Now

$$\frac{d\pi}{dn_g} = 0, \text{ when } \frac{P \lambda N}{RT(N + n_g)^2} = \frac{1}{V_L}, \text{ that is, when}$$

$$n_g = \sqrt{\frac{V_L P \lambda N}{RT}} - N. \quad (21)$$

This value of n_g must denote a maximum because

$$\frac{d_2 \pi}{dn_g^2} = - \frac{2P\lambda N}{RT(N + n_g)^3},$$

which must be negative for all real values of n_g .

Equation (14) may be written

$$\frac{dn_g}{dA} = K_2 \left(\frac{n_g^2 - \left(\frac{V_L P \lambda}{RT} + \Delta - N \right) n_g - N \Delta}{V_L(N + n_g)} \right),$$

but

$$\frac{d\pi}{dA} = \frac{d\pi}{dn_g} \times \frac{dn_g}{dA},$$

therefore

$$\frac{d\pi}{dA} = K_2 \left(\frac{n_g^2 - \left(\frac{V_L P \lambda}{RT} + \Delta - N \right) n_g - N \Delta}{V_L(N + n_g)} \right) \left(\frac{P \lambda N}{RT(N + n_g)^2} - \frac{1}{V_L} \right). \quad (22)$$

So that $\frac{d\pi}{dA} = 0$

when

$$n_g = \sqrt{\frac{V_L P \lambda N}{RT}} - N \quad \text{from Equation 21}$$

or

$$n_g = \alpha \text{ or } \beta \quad \text{from Equation (18)}$$

or

$$n_g = \frac{V_L P \lambda}{RT} - N \quad \text{from Equation (17)}$$

Of these the last two conditions denote minima which can occur only at the ends of the tower; therefore, π passes through a maximum but never through a minimum throughout the length of the tower.

Values of the Adeney and Becker Function According to Donnan and Masson's Equation

On differentiation, the Donnan and Masson equation

$$\pi = \pi_1 e^{k_2 \left(\frac{1}{V_L} - \frac{k}{V_g} \right) A}$$

becomes

$$\frac{d\pi}{dA} = k_2 \left(\frac{1}{V_L} - \frac{k}{V_g} \right) \pi_1 e^{k_2 \left(\frac{1}{V_L} - \frac{k}{V_g} \right) A} \quad (23)$$

which may be directly compared with Equation (22).

It can be seen from Equation (23) that

$$\frac{d\pi}{dA} = 0, \text{ when } A = \pm \infty \text{ or } \frac{1}{V_L} = \frac{k}{V_g}.$$

When $A = \pm \infty$ the tower cannot be real, and it has been shown that when $\frac{1}{V_L} = \frac{k}{V_g}$, π remains constant throughout the tower, therefore no maximum is possible from this equation.

If the function $\pi = f(A)$ be plotted, it will be seen that the Donnan and Masson equation predicts that the π curve will be either parallel to the A -axis or convex towards it, since if $\frac{1}{V_L} > \frac{k}{V_g}$, $\frac{d\pi}{dA}$ will increase with A , while if $\frac{1}{V_L} < \frac{k}{V_g}$, $\frac{d\pi}{dA}$ will decrease as A increases. Hence it would be expected that there would be a maximum discrepancy between the two formulas in any tower where n_o could have the value $\sqrt{\frac{V_L P \lambda N}{RT}} - N$.

Numerical Examples

This has been illustrated by the working out of eight hypothetical cases for towers absorbing carbon dioxide under different conditions.

TABLE I
WATER RATES

| Case | Cu. m. per hr. |
|------|-------------------|
| A | 2.2 |
| B | 2.5 |
| C | 3.0 |
| D | 4.0 |
| E | 5.5 |

(1) Five cases (A to E) in which a gas containing 30% of carbon dioxide is scrubbed down to 1% of carbon dioxide by varying the water rate and interfacial area. In each case the inlet gas rate is fixed at 100 cu. m. per hr., the temperature at 20° C. and the pressure at 50 atm. The inlet water is assumed to contain no carbon dioxide.

The water rates are shown in Table I.

Cases A to D are represented graphically below, and the difference in the curves predicted by the two formulas can be clearly seen.

(2) In Case (F) a gas containing 5% of carbon dioxide is supposed to be scrubbed down to 0.2% at atmospheric pressure by 109 cu. m. per hr. of water. The gas rate was again 100 cu. m. per hr.

(3) In Cases (G) and (H) the same gas is supposed to be scrubbed down to 0.5% of carbon dioxide by 110 and 109 cu. m. per hr. of water respectively, with an inlet gas rate of 100 cu. m. per hr.

TABLE II
MEAN DRIVING FORCE

| Case | I Donnan and Masson | II Equation (19) | $\frac{II - I}{I} \times 100$ % difference |
|------|---------------------------|------------------------|--|
| A | 0.1014 | 0.035 | 207 |
| B | 0.042 | 0.064 | 52.4 |
| C | 0.0639 | 0.094 | 45.6 |
| D | 0.0815 | 0.11 | 35.0 |
| E | 0.1315 | 0.163 | 23.9 |
| F | 0.0000529 | 0.00006675 | 26.2 |
| G | 0.0001692 | 0.000186 | 9.95 |
| H | 0.0001642 | 0.0001774 | 7.85 |

Values obtained from Donnan and Masson's formula and from Equation (19) for the mean driving force are given in Table II.

It would seem from the foregoing analysis that the error introduced into the Donnan and Masson formula by their assumption of the constancy of the gas volume is not likely to be very serious in any practice where the interfacial area is reasonably

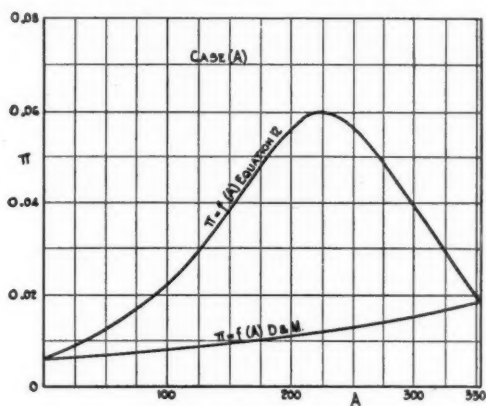


FIG. 1

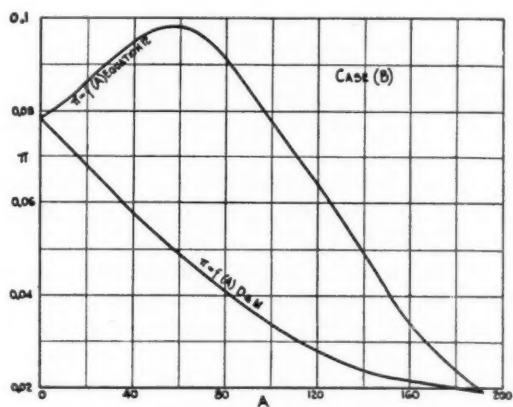


FIG. 2

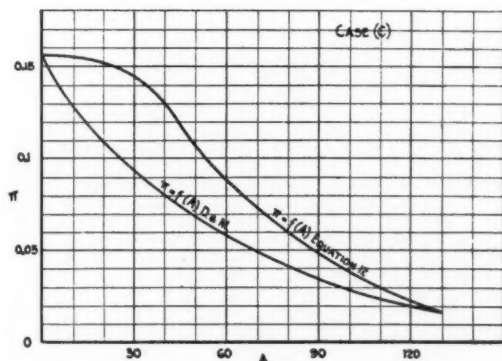


FIG. 3

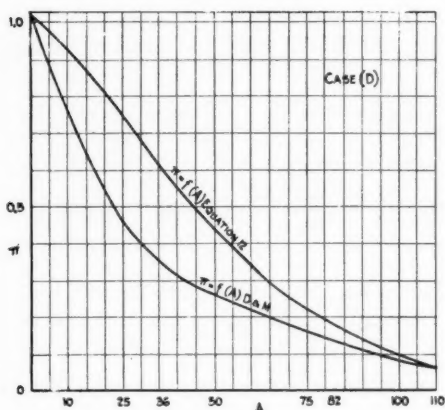


FIG. 4

small and the tower is not highly efficient, *i.e.*, where equilibrium between the ingoing gas and effluent liquor is not closely approached. In this case it would seem that the Donnan and Masson formula should be reasonably accurate. This accounts for the wide success of the formula in practice even in cases where the volume of gas washed out was considerable. Donnan and Masson assumed that when considerable percentages of gas were absorbed in the tower their formula would be inaccurate. It is, in general, true that the higher the percentage of soluble gas, the less accurate Donnan and Masson's equation becomes, but an even more important factor is the degree of closeness to equilibrium under which the tower is operated. If the tower is run near to equilibrium the error will be great, and Donnan and Masson's formula may prove to be more inaccurate in such a case than when it is applied to a case in which a larger percentage of gas is washed out. This is illustrated by Cases (E) and (F). The error is greater in Case (F), where only 4.8% of the gas is absorbed, than in Equation (3) where 29% of the gas is absorbed.

In general it can be said that the Donnan and Masson formula has a fair chance of proving accurate except when

$$n_{g1} > \sqrt{\frac{V_L P \lambda N}{RT}} - N > n_{g2}$$

in any tower.

These results may prove to be of use in practice, but the chief value of the above analysis consists in the fact that it has produced a kinetic expression that corresponds with the predictions of thermodynamics, and therefore removes an apparent contradiction in the theory of this subject.

NOTE:—In eliminating the conditions

$$(1) \quad \left(\frac{V_L P \lambda}{RT} + \Delta - N \right)^2 < |4N\Delta| \quad \text{when } \Delta \text{ is negative}$$

and

$$(2) \quad \left(\frac{V_L P \lambda}{RT} + \Delta - N \right)^2 = |4N\Delta|$$

the argument was used that $\lambda C_g - C_L$ could never be negative in an absorption tower. This is, of course, true for absorption towers but untrue for regeneration towers, that is, towers in which a soluble gas is forced out of a liquid by a current of air or inert gas. These two rejected solutions might be of use in such a case. They are obtained as follows:

Case (1)

Let $D = -\left(\frac{V_L P \lambda}{RT} - \Delta - N\right)$, then Equation (10) becomes,

$$\begin{aligned} AK_2 &= V_L \int \frac{1/2(2n_g + D) + N - 1/2D}{n_g^2 + Dn_g + N\Delta} dn_g + \text{constant} \\ &= V_L \int \frac{(N + 1/2D)dn_g}{n_g^2 + Dn_g + N\Delta} + \frac{V_L}{2} \log_e (n_g^2 + Dn_g + N\Delta) + \text{constant}. \end{aligned}$$

Now, let $E = \sqrt{N\Delta - 1/2D^2}$, then we have,

$$AK_2 = \frac{V_L(N - 1/2D)}{E} \tan^{-1} \frac{N + 1/2D}{E} + \frac{V_L}{2} \log_e (n_g^2 + Dn_g + N\Delta) + \text{constant}.$$

Case (2)

The solution of Equation (10) for this case is

$$AK_2 = \frac{V_L(N - 1/2D)}{n_g + 1/2D} + \frac{V_L}{2} \log_e (n_g^2 + Dn_g + N\Delta) + \text{constant}.$$

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SORPTION OF DEUTERIUM OXIDE BY CELLULOSE¹

By T. KING² AND C. OUELLET³

Abstract

The sorption of deuterium oxide by cellulose at 23.4° C. was investigated over the whole range of vapor pressures and found to show the same characteristics as that of water. The molar quantities sorbed at a given pressure are equal, and the kinetic curves exhibit the same features. After desorption of deuterium oxide, a small but permanent increase in the weight of the cellulose was observed. This suggested an exchange reaction between deuterium and hydrogen atoms.

Introduction

A preferential sorption of deuterium oxide from heavy water of various concentrations has been reported by Washburn and Smith (9) and by King and co-workers (4). These investigators used charcoal and silica gel as sorbents. The aim of the experiments dealt with in the present paper was to find whether a similar effect exists in the case of cellulose. This was done by comparing the sorption isotherms obtained with water vapor and with deuterium oxide vapor 99.2% pure.

As is well known from the work of Pidgeon and Maass (6), Sheppard and Newsome (7) and Filby and Maass (2), the sorption isotherm of water by cellulose is an S-curve, showing normal Langmuir adsorption at the lower pressures and rising to much higher values as the saturation pressure is approached. This latter part of the curve has been attributed both to condensation and to the uncoupling of residual valencies, resulting in an increased capacity for sorption. It was felt that a selective sorption of deuterium oxide with respect to water in this region might throw new light on the problem.

Experimental Method

The writers used the direct method, which consists in measuring the increase in weight of a sample of cellulose caused by the sorption of a vapor. This was done by means of quartz balances constructed according to the directions of McBain and Bakr (5) from quartz fibres of maximum diameter 0.2 mm. and from 4 to 6 ft. long. The fibres were made by pulling rapidly, in the oxy-acetylene flame, quartz rods 4 mm. in diameter, which were then wound into spirals by turning them on a carbon rod 12 mm. in diameter, while heating at the point of contact with a small flame. On calibration with small known weights, all the spirals used gave a straight line passing through the origin when the deflection was plotted against the weight. This showed that they obeyed Hooks' law. The three spirals employed showed a deflection of 1 mm. when supporting weights of 0.0056, 0.0059 and 0.0087 gm., respectively. A cathetometer, reading to 0.01 mm., was used. Hence a variation in weight of 0.00006 gm. could be detected.

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The apparatus, as shown in Fig. 1, consisted of three glass tubes, B_1 , B_2 , B_3 , 45 cm. long and 5 cm. in diameter, provided with ground glass joints and containing the spirals to which samples of cellulose were attached by glass hooks. These tubes were connected to a side-tube, V , containing the liquid, the vapor of which was adsorbed, and, through a phosphorus pentoxide tube and a trap, T , to the evacuating system consisting of a mercury diffusion pump, Hyvac pump, manometer and McLeod gauge. To keep the temperature constant, the sorption tubes were immersed in a water bath, the

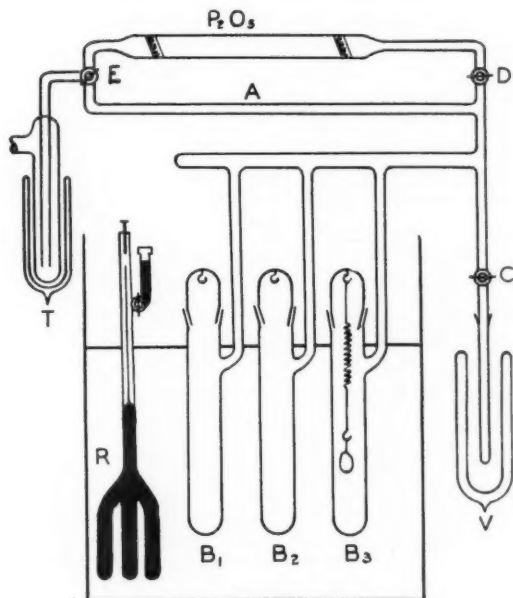


FIG. 1. Sorption apparatus.

temperature of which was controlled by a mercury thermoregulator, R , made of Pyrex glass and having three prongs to ensure compactness and quick establishment of equilibrium owing to the large volume-surface ratio. A useful improvement consisted in adding a side tube provided with a stopcock, so that the regulator could be used over a wide range of temperatures by adding or removing mercury. The temperature of the bath was kept constant to within 0.01°C. over periods of several weeks.

The required vapor pressures of water were obtained by keeping the tube V at constant known temperatures in a vacuum flask filled with compounds of definite melting points. A small thermostat was used to control temperatures above 15.4°C. The vapor pressures corresponding to the different temperatures were taken from the Critical Tables. In the case of deuterium oxide, however, no experimental data being available for the temperatures used, the vapor pressures between -25°C. and $+23.5^\circ \text{C.}$ were calculated

from the equation of Topley and Eyring (8), which gives the ratio of the vapor pressures of deuterium oxide and water as a function of the absolute temperature, T .

$$\frac{P_{\text{D}_2\text{O}}}{P_{\text{H}_2\text{O}}} = 1.35 e^{-\frac{288}{RT}}$$

The calculated values of $P_{\text{D}_2\text{O}}/P_{\text{H}_2\text{O}}$ and $P_{\text{D}_2\text{O}}$ for the temperatures used in this work are given in Columns 3 and 4 of Table I.

The writers used "Standard Cellulose" containing 99.5% α -cellulose, as prepared by the International Paper Company and supplied through the courtesy of Mr. R. Samson. The heavy water, containing 99.2% D_2O (density = 1.1049 at 20° C.) was received as a sample from the Norsk Hydro Elektrisk Kvaeltotaktieselskab.

The experimental procedure was as follows: After the balances carrying the samples had been set in place, 1 to 2 cc. of water or deuterium oxide was introduced into V , and the liquid freed of dissolved gases by freezing and evacuating several times until no difference of pressure was noted on the McLeod gauge. Tap C was then closed and the system evacuated through the phosphorus pentoxide tube, T and V being kept at the temperature of an ether and solid carbon dioxide mixture; after 12 to 24 hr. no change was observed in the readings of the balances or the McLeod gauge. This final reading was taken as the "dry weight" of the cellulose. The pumping system was then cut off by closing taps D and E , and the vapor allowed to diffuse through C from the liquid at a definite temperature in V . Cathetometer readings were taken from time to time until no further increase in the weight of the cellulose was observed. This required periods ranging from three hours at the lower pressures to 24 and even 48 hr. at the higher ones, as already noticed by Filby and Maass (2).

Results

In order to test the behavior of the apparatus and materials, and obtain a firsthand basis for comparison, the writers repeated the measurement of the sorption of water. The results are shown in Fig. 2. The results, obtained at 23.4° C., are in close agreement with those of Filby and Maass (2) at 20.0° C., provided that the pressures are expressed in each case as fractions of the maximum vapor pressure of water at the temperature of the experiment. These relative vapor pressures are designated in this paper by "R.v.p." and expressed on a percentage basis. Desorption brought the weight of the cellulose back to its initial value within the limits of accuracy of the writers' measurements.

The sorption of deuterium oxide exhibits the same features as that of water, as can be seen from Fig. 2. Table I gives the detailed data including the calculated per cent R.v.p. of deuterium oxide at the different temperatures used, and the times in hours after which the final readings were taken. The amounts of deuterium oxide sorbed are given in percentage of the dry weight

of the sample. The ratio of the sorbed weights of deuterium oxide and water is virtually constant and roughly equal to that of the molecular weights of the two substances.

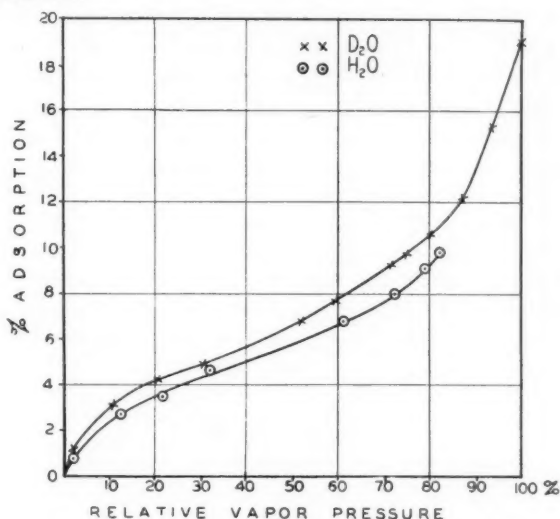


FIG. 2. Sorption isotherms of water and deuterium oxide.

TABLE I

SORPTION OF DEUTERIUM OXIDE BY CELLULOSE AT 23.4° C.

| Time, hr. | Temp., °C. | $\frac{P_{D_2O}}{P_{H_2O}}$ | P_{D_2O} mm. of Hg | % R.v.p. | % sorption |
|-----------|------------|-----------------------------|----------------------|----------|------------|
| 4 | -25.0 | 0.798 | 0.38 | 2.00 | 1.07 |
| 3 | -7.5 | 0.827 | 2.01 | 10.61 | 3.06 |
| 48 | 0.0 | 0.837 | 3.84 | 20.26 | 4.13 |
| 24 | 5.3 | 0.846 | 5.65 | 29.87 | 4.54 |
| 24 | 13.2 | 0.857 | 9.75 | 51.51 | 6.86 |
| 24 | 15.2 | 0.859 | 11.13 | 58.80 | 7.69 |
| 24 | 18.2 | 0.863 | 13.52 | 71.42 | 9.31 |
| 24 | 18.9 | 0.864 | 14.15 | 74.71 | 9.84 |
| 48 | 20.0 | 0.866 | 15.18 | 80.17 | 10.65 |
| 24 | 21.3 | 0.867 | 16.47 | 87.01 | 12.37 |
| 24 | 22.4 | 0.869 | 17.65 | 93.24 | 15.36 |
| 24 | 23.4 | 0.872 | 18.93 | 100.00 | 19.09 |

After desorption, however, the weight of the cellulose did not return to its original value, but a slight excess of weight amounting to 0.59% was noted. Deuterium oxide vapor was again admitted at about 80% R.v.p. and left in the apparatus for three days. On desorbing again it was found that the residual weight had now gone up to a value of 0.87% above that of the dry cellulose. Although this experiment has not been carried further, it appears reasonably certain that the "dry weight" (as defined experimentally) increases gradually in the presence of heavy water.

In Fig. 3 are shown the results of measurements of the velocity of sorption of deuterium oxide at three vapor pressures. The initial rate of sorption at very low pressures was too high to be measured. The equilibrium value ultimately reached at one pressure was used as a starting point for the next curve. These values were 3.06, 4.13, 4.84 and 5.90% sorption, corresponding to 10.6, 20.3, 29.9 and 42.0% R.v.p., respectively. A serious cause of error

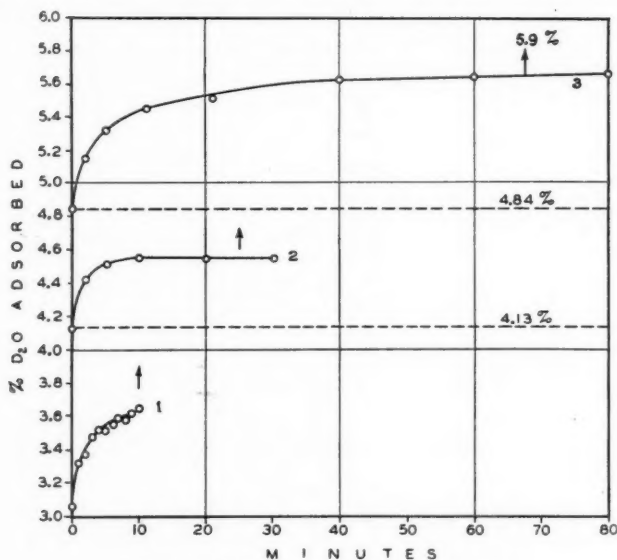


FIG. 3. Rate of sorption of deuterium oxide.

arises from the fact that, on starting a run, the establishment of a new vapor pressure in the large volume constituted by the sorption tubes suffers a certain delay, depending upon the rate of diffusion and formation of fresh vapor from the liquid in *V*. However, it can be seen from the curves that the sharp initial rise is followed by a much slower process, resulting in a false appearance of early saturation.

Discussion of Results

From the data given, the writers conclude that the sorption of deuterium oxide by cellulose at 23.4° C. is, over the entire range of vapor pressures, very similar to that of water. Both follow a normal adsorption isotherm, which, as the pressure approaches saturation, changes into a rapidly rising curve, showing that a new process sets in. It may be suggested here that, if this were due to condensation, it could be expected to take place at a somewhat lower relative vapor pressure in the case of deuterium oxide than in that of water. The writers' results give no indication of such a difference. In fact, comparing at different pressures the weights of deuterium oxide and

water taken up by the cellulose, the writers find that the ratio oscillates between 1.08 and 1.14, whilst the ratio of the molecular weights is 1.11. The molar quantities sorbed are thus equal. The velocity of sorption also exhibits the same peculiarities in both cases.

The permanent increase in weight of the cellulose after desorption was, unfortunately, not thoroughly investigated. It may be due either to some irreversible sorption or to an exchange reaction between deuterium and hydrogen atoms. In view of the numerous cases in which such reactions have been found to take place in similar compounds, the writers favor the latter hypothesis (1, 3). The reaction takes place very slowly, the total effect amounting to only 0.87% after several days. This would correspond to the substitution by deuterium of 0.8 of one of the ten hydrogen atoms in the elementary formula of cellulose. But there is no indication that the reaction was complete. Should it be possible to follow this reaction until some sort of saturation is reached, one could determine, from the number of hydrogen atoms substituted, which group or groups are affected.

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